STUDIES IN CHLOROSULPHURIC ACID SOLVENT SYSTEM

A THESIS

SUBMITTED TO THE ALIGARH MUSLIM UNIVERSITY, ALIGARH
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Certified that the work embodied in this thesis entitled "Studies in Chlorosulphuric Acid Solvent System" is the result of the original researches carried out under my supervision by Mr. Zafar Ahmad Siddiqi and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University.

(S.A.A. Zaidi)
Reader in Chemistry

A C K N O W L E D G E M E N T

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Zafar Ahmad Siddiqi.

Zafar Ahmad Siddiqi

C O N T E N T S

P U B L I C A T I O N

1. Ionization of ureas, carbazides and carbazones in chlorosulphuric acid.
   Journal of Inorganic and Nuclear Chemistry (in press)

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A B S T R A C T

The behaviour of a large number of different types of compounds acting as bases in chlorosulphuric acid solvent system has been studied. Conductometric, n.m.r. and u.v. spectroscopic studies in chlorosulphuric acid solutions of urea, thiourea and on some of their substituted derivatives have been carried out. It has been found that urea and thiourea are monoprotonated whereas the biureas and cyanoacetylurea are diprotonated. Changes in the basicity of the compounds due to the inductive effect of the substituents have been noted. For solutions of N-allylthiourea, N,N'-diisopropylthiourea and 1,3-diphenylthiourea the conjugate acid proton ($C=SH^+$) peak has been observed in the n.m.r. spectra indicating protonation at sulphur atom in these compounds. For thiourea and 2,5-dithiobiurea the conjugate acid proton peak could not be observed essentially due to exchange with the solvent proton. However, in both the cases the NH_2 and NH groups were found unattacked by the acid proton providing evidence that protonation in these compounds occurs at sulphur atom. For urea and its substituted derivatives in HSO_3Cl no peak due to conjugate acid proton has been observed in the n.m.r.

spectra. For biourea and cyanoacetylurea, however, the appearance of unaffected NH and NH_2 protons peaks suggest that protonation in these compounds might be occurring at oxygen atom of the carbonyl group. Ultraviolet spectroscopic studies on solutions of ureas and thioureas support oxygen or sulphur protonation of these compounds in chlorosulphuric acid.

From conductometric studies on solutions of a few substituted carbazides, carbazones and their thio analogues in HSO_3Cl it has been found that except phenylsemicarbazide which undergoes monoprotonation all the other derivatives undergo partial diprotonation on oxygen or sulphur and on nitrogen atom. The $C=OH^+$ proton peak could not be observed in the n.m.r. spectra of these compounds due to a rapid exchange with solvent proton. However, for the thio analogues the conjugate acid proton ($C=SH^+$) has been observed. Protonation at nitrogen atom also has been indicated by the appearance of peaks attributable to the protonated nitrogen atoms. Ultraviolet spectroscopic studies also support protonation on oxygen or sulphur atom in these compounds.

From conductance measurements on solutions of a few hydrazines in HSO_3Cl it has been found that phenylhydrazine and 4-nitrophenylhydrazine undergo complete diprotonation

while for 2-nitrophenylhydrazine a partial diprotonation is indicated. The extent of protonation in 2,4-dinitrophenylhydrazine and 2,5-dichlorophenylhydrazine is substantially lower as compared to that in phenylhydrazine and only monoprotonation has been observed in this case. Hydrazine sulphate ionizes producing diprotonated hydrazine (NH_3^+-NH_3^+).

From conductometric studies on solutions of oxides of As, Sb, Bi, P, V, Se and Te and on oxyhalides of Sb, Bi, P and V in FSO_3Cl, it has been found that trioxides of As, Sb and Bi form corresponding oxychlorosulphates. Oxyhalides of Sb and Bi also form their oxychlorosulphates. The oxychlorosulphates of antimony and bismuth presumably ionize partially to produce the hithertofore elusive oxycations SbO^+ and BiO^+. The dissociation constant of the oxychlorosulphates of antimony and bismuth formed from ionization of trioxides as well as oxyhalides has been calculated and found to be very nearly the same in both the cases.

Phosphorus pentoxide forms protonated phosphoric acid while phosphoryl chloride has been found to be incompletely protonated. The basic ionization constant of conjugate acid of phosphoryl chloride has been calculated.

Vanadium pentoxide and vanadyl chloride behave as weak electrolytes and presumably form $[VO(SO_3Cl)_3]$. The pentoxide of As, Sb and Nb do not react with the acid and

remain insoluble in it. The dioxides of selenium and tellurium behave as simple strong bases and are protonated. The extent of protonation in TeO_2 is greater than in SeO_2.

Conductometric, n.m.r. and i.r. spectroscopic studies have been carried out on solutions of a few carboxylic acid anhydrides in chlorosulphuric acid. It has been found that acetic and benzoic anhydrides behave as strong base and form only carboxylic acidium ion ($RCO_2H_2^+$). The dicarboxylic acid anhydrides viz.succinic, phthalic, 3-nitrophthalic and maleic anhydrides have been found to behave as weak bases in HSO_3Cl and presumably form the corresponding intramolecularly hydrogen bonded protonated anhydride. The basic ionization constant of their conjugate acid has been calculated.

CHAPTER - I

I N T R O D U C T I O N

INTRODUCTION

It is quite well-known that the solvent plays an important role in deciding the course of most of the chemical reactions. Until the turn of the century the chemical reactions were mainly carried out in aqueous medium. However, with the growing realization that the influence of the solvent could indeed be profound, several reactions which were earlier not feasible in aqueous medium have been successfully carried out in other suitable solvent. By judicously changing the solvent the products from a given set of reactants have been completely changed and in some cases reactions have even been reversed. During the last half a century or so a variety of non-aqueous solvents have come to be used with great advantage. Liquid ammonia, liquid sulphurdioxide, liquid hydrogen fluoride and sulphuric acid are to name only a few distinguished ones. Studies in these media have not only broadened the scope of synthetic chemistry but also have increased the number and type of theoretical studies that may be carried out in them. For example, liquid hydrogen fluoride and bromine trifluoride have been found to be good fluorinating agents and a good deal of new

fluorine compounds many of which possess industrially important properties have been synthesized. These two solvents have also been found to be good ionising ones for a variety of organic and inorganic compounds which have been investigated. The non-aqueous solvents have been classified into three major classes viz., protonic, aprotic and coordinating solvents. The protonic solvents include the strong ionizing acidic media e.g, liquid hydrogen halides, sulphuric acid, fluorosulphuric acid, disulphuric acid and selenic acid etc. Liquid sulphurdioxide is a typical example of an aprotic solvent and various types of reactions like solvolysis, oxidation reduction, metathesis and complex formation have been studied in this solvent. It has been shown that dimethyl formamide, dimethyl acetamide, acetonitrile, pyridine and phosphoryl chloride act as coordinating solvents through the lone pair electrons at oxygen or sulphur atom.

The chlorosulphuric acid solvent system which concerns the present work belongs to the class of protonic solvents and is one of the stronger acidic media for chemical reactions. A very brief review of the researches done in this kind of media are given in the following paragraphs.

Because of the high acidity of sulphuric, fluorosulphuric and disulphuric acids most of the compounds have been found to behave as bases in these solvents. It has been shown that organic compounds with even weakly basic functional groups like ketones, nitro compounds, ethers, sulphoxides, sulphides, sulphones, amides, carboxylic acids and their anhydrides undergo protonation in these media.[1] A variety of organic and inorganic cationic species like carbonium ions, halogen and interhalogen cations viz., I_3^+, I_5^+, IO^+ and ICl_2^+ and a few oxycations NO^+ and NO_2^+ which are under normal conditions unstable species have been shown to be stabilized in the above mentioned media.[1,2] It has been shown that S, Se, Te, P, As and Sb can be oxidized in solutions[3-10] in H_2SO_4, $H_2S_2O_7$ and HSO_3F to polyatomic cations containing the element in low valency states. The existence of the ions Se_8^{2+}, Se_4^{2+}, Te_4^{2+}, S_{16}^{2+}, S_8^{2+} and S_4^{2+} in solutions has been established by a combination of cryoscopic, conductometric, spectroscopic and magnetic measurements.[11-14] It has been indicated that Se_4^{2+} and Te_4^{2+} have a square planar structure while S_8^{2+}, Se_8^{2+}, Te_8^{2+} ions have the bicyclic structure.[15] Recently Gillespie and coworkers[16] have shown that the acidity of fluorosulphuric acid can be further enhanced

by the addition of antimony pentafluoride and sulphur trioxide. The 1:3 mixture of antimony pentafluoride and sulphur trioxide in fluorosulphuric acid resulted in the formation of SbF_5-$3SO_3$-HSO_3F or $SbF_2(SO_3F)_3$-HSO_3F which has been termed as super acid system. This super acid system has been found useful for the preparation of cations of chlorine and bromine which are even stronger Lewis acids than iodine cations and a few compounds of these cationic species have also been synthesized.[17,18]

The use of chlorosulphuric acid as a non-aqueous ionizing solvent has however, not been much explored. It was Walden[19] who determined the specific conductance of chlorosulphuric acid and suggested it to be a good ionising solvent. Barr[20] and Waddington[21] and their coworkers found that chlorosulphuric acid behaves as a weak acid in 100% H_2SO_4 and liquid HCl. From the conductometric studies on solutions of a few inorganic and organic compounds in chlorosulphuric acid[22] the following self-ionization of the acid has been suggested:

$$HSO_3Cl \rightleftharpoons H^+ + SO_3Cl^- \qquad (1)$$

Recently Robinson and Ciruna[23] have carried out conductometric, transport and density measurements on

solutions of alkali metal chlorides, alkaline earth metal chlorides and their chlorosulphates. They have further made conductometric measurements on solutions of a few organic solutes which include acetic acid, benzoic acid, p-aminobenzoic acid and p-phenylene diamine in this solvent. They have confirmed the mode of self-ionization for the acid represented by equation(1) and have indicated that alkali metal chlorides and their chlorosulphates behave as strong electrolytes and ionise according to equation(2) and (3) as given below:

$$MCl + HSO_3Cl \rightleftharpoons M^+ + SO_3Cl^- + HCl \qquad (2)$$

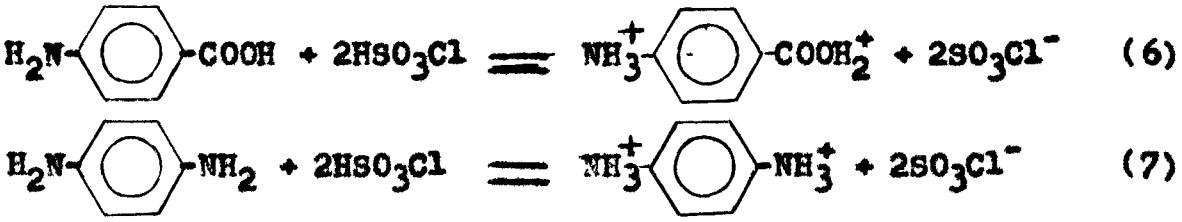
$$MSO_3Cl \rightleftharpoons M^+ + SO_3Cl^- \qquad (3)$$

M = alkali metals

Organic solutes in HSO_3Cl behave as simple bases and it has been suggested that monoprotonation occurs in acetic acid and benzoic acid whereas p-aminobenzoic acid and p-phenylenediamine are diprotonated as given by the following reactions:

$$CH_3COOH + HSO_3Cl \rightleftharpoons CH_3COOH_2^+ + SO_3Cl^- \qquad (4)$$

(5)



(6)

(7)

Tetra chlorides of selenium and tellurium have also been found to ionise completely producing the cationic species $SeCl_3^+$ and $TeCl_3^+$ respectively[24] according to the reaction:

$$SeCl_4 + HSO_3Cl \rightleftharpoons SeCl_3^+ + SO_3Cl^- + HCl \quad (8)$$

$$TeCl_4 + HSO_3Cl \rightleftharpoons TeCl_3^+ + SO_3Cl^- + HCl \quad (9)$$

The formation of the cationic species $SeCl_3^+$ and $TeCl_3^+$ in solution was for the first time revealed in HSO_3Cl which were later also prepared in the other highly acidic solvents like $H_2S_2O_7$[25] and HSO_3F.[26]

It is, therefore, clear that chlorosulphuric acid is a suitable solvent for the study of the behaviour of organic as well as inorganic compounds and also for stabilising the less stable cationic species. Unfortunately, lesser interest has been shown in the use of this solvent as a non-aqueous ionising medium. It was, therefore, considered worthwhile to investigate the behaviour of a

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few organic and inorganic compounds and also to expand the scope and suitability of this solvent in stabilizing a few cationic species.

It seems appropriate here to review briefly the physical properties of this solvent. The various physical constants of chlorosulphuric acid are listed in Table -1 and have been discussed in the following few lines.

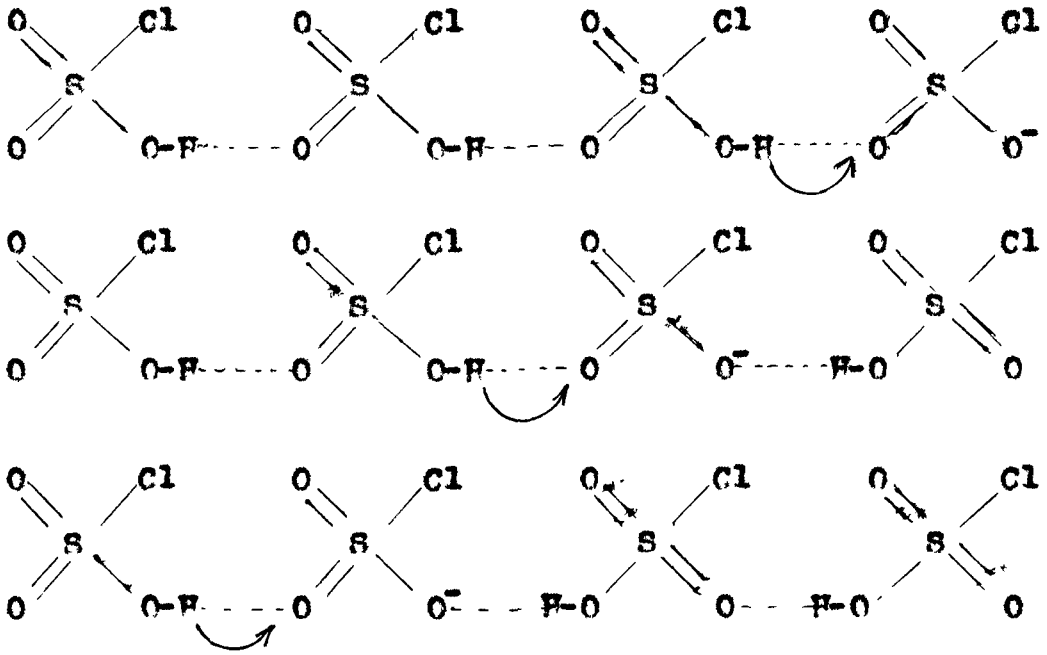
While the relatively low freezing point of chlorosulphuric acid as compared to that of sulphuric acid may enable one to study by n.m.r. spectroscopy the protonation of bases at sufficiently low temperature at which the proton exchange between the solvent and the conjugate acid is minimised, it precludes the cryoscopic studies of its solutions.

TABLE - 1

Some physical properties of FSO_3Cl

		References
Boiling point	62°C at 2.7 m.m.	(27)
	78°C at 21.5m.m.	(17)
	152°C at 760 m.m.	(27)
Freezing point	-80°C	(27)
Density	1.741 $gm.ml^{-1}$	(30)
Viscosity (25°C)	0.0243 P	(28)
Dielectric Constant (14°C)	60 ± 10	(29)
Molar susceptibility	46.60	(30)
Specific heat	0.282 $cal.gm^{-1}$	(31)
Hammett acidity value	-12.78	(32)

One of the important characteristics of this solvent is that in solutions most of the current is carried by the anion of solvent self-dissociation SO_3Cl^- which conducts by an abnormal proton transfer mechanism.[23] This arises from a Grothus-type chain mechanism in which protons are transferred along chains of solvent molecules as shown in the following diagram.



The dielectric constant of chlorosulphuric acid (ϵ = 60) as compared to sulphuric acid (ϵ = 100) and fluorosulphuric acid (ϵ = 120) is relatively low. This would

possibly encourage the formation of ion pairs specially in the case of cations of small ionic radii. The concentration of free chlorosulphate ions (which are mainly responsible for conducting current) would thus be reduced and consequently there would be a decrease in the specific conductivities of the solutions. Formation of ion pairs in the solutions of strontium and calcium chlorides and chlorosulphates has been proposed accounting for the low specific conductivities of these solutions[23] compared to that of a dibasic standard.

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PRESENT WORK

There has been much controversy regarding the actual site of protonation in compounds containing bi-functional groups like amides, ureas and their thio analogues having both oxygen or sulphur atoms as well as nitrogen atom susceptible for proton attack in acidic media.[33-35] Studies on a few amides in sulphuric and fluorosulphuric acids[36-38] have recently been made and it has been proposed that in dilute sulphuric acid N-protonation predominates whereas in concentrated acids O-protonated species are formed. However, recently some doubts have been raised about N-protonation of amides even in dilute acids.[39-42] It, therefore, appeared to be of interest to examine the behaviour of substituted ureas and thioureas with a view to determining the site and extent of protonation and also the effect of substitution on the basicity of these compounds in chlorosulphuric acid.

Carbazides, carbazones and their thio analogues also have several functional groups containing both nitrogen and oxygen or sulphur atoms and their behaviour has not been investigated in strong acidic media. It, therefore, seemed worthwhile to examine the mode of ionization and basicity of these compounds in chlorosulphuric acid.

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From conductometric studies on solutions of phenylhydrazine in fluorosulphuric[26] acid and of hydrazine dihydrochloride in chlorosulphuric acid[23] it has been shown that they behave as bases in these highly acidic media. However, the basicity of substituted phenylhydrazines in strong acedic media is not known. In the present work the investigation of the behaviour of hydrazine sulphate and a few substituted phenylhydrazines in chlorosulphuric acid has been undertaken with a view to determining their relative basicities.

Evidence for the existence of oxycations NO^+ and NO_2^+ responsible for nitration in synthetic organic chemistry has come from studies on solutions of the anhydrides and halides of the oxyacids of nitrogen in strong acidic media.[43-46] Attempts to prepare other oxycations of the elements of the same group were successful only in the case of AsO^+ which was obtained by the ionization of As_2O_3 in H_2SO_4.[47] It, was, therefore of interest to explore the possibility of the formation of oxycations of As, Sb, Bi, P and V in chlorosulphuric acid from the ionization of oxides as well as oxyhalides of these elements.

| 2

The carboxylic acid anhydrides ionize in strong acidic media in different modes e.g; while acetic anhydride has been found to dehydrate sulphuric acid[48] to form the carboxylic acidium ion ($CH_3CO_2H_2^+$), in disulphuric acid[46] and in super acid[49], HSO_3F-SbF_5-SO_2, it ionizes to form the acyl ion (CH_3CO^+). The ionization of dicarboxylic acid anhydrides in strong acids has not been fully studied. The author was, therefore, prompted to study the behaviour of a few carboxylic acid anhydrides in chlorosulphuric acid with a view to determining the mode and extent of ionization and to identifying the species being formed.

CHAPTER - II

EXPERIMENTAL METHODS IN CHLOROSULPHURIC ACID

EXPERIMENTAL METHODS IN CHLOROSULPHURIC ACID

The following experimental methods have been used to study the behaviour of solutes in chlorosulphuric acid

1. Electrical Conductivity
2. Spectroscopy

   (a) Ultra-Violet and Visible Spectra

   (b) Nuclear Magnetic Resonance Spectra

   (c) Infrared Spectra

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Electrical Conductivity Measurements

The specific conductance of a solution is defined as the reciprocal of its specific resistance symbolized by

$$\mathcal{K} = \frac{1}{r} \qquad (10)$$

where r = specific resistance.

since $R = r \frac{1}{a}$ ohms. (11)

Substituting r from equation(10) into (11),

$$\mathcal{K} = \frac{1}{R} \frac{1}{a} \text{ ohm.}^{-1}\text{cm.}^{-1} \qquad (12)$$

Where R is the resistance and $(\frac{1}{a})$ is the cell constant.

For a solution containing ionic species 1,2,3....i of concentrations C_1, C_2, C_3 ..... C_i moving under a potential gradient of one volt per centimeter the velocities of the ions U_1, U_2 .... U_i are defined as "absolute ion mobilities". The relation between the absolute ion mobilities of the ions of an electrolyte in solution with its specific conductance $\mathcal{K}$ is given by the expression

$$\mathcal{K} = \frac{F}{1000} \sum_i C_i Z_i U_i \qquad (13)$$

where Z_i is the charge carried by the ith ion and F is the Faraday constant.

Incorporating Faraday constant into general expression it becomes-

$$\kappa = \frac{1}{1000} \sum_i c_i z_i \lambda_i \qquad (13)$$

where $\lambda_i = F U_i$ the ionic mobility and κ is the specific conductance in $ohm.^{-1}cm.^{-1}$

The Cell Constant: For a given cell the ratio l/a where l is the distance between the electrodes in cm. and a is the effective "area" of each electrode in $cm.^2$, is defined as the cell constant represented by G then

$$G = R.\kappa \qquad (14)$$

Where κ and R as already defined above are specific conductance and resistance of the solution respectively.

Determination of Cell Constant: Following Jones and Bradshaw[50] cell constants are determined by using a potassium chloride solution of known specific conductance found from measurements in cells of known dimensions. However, since the specific conductance of minimum conducting sulphuric acid

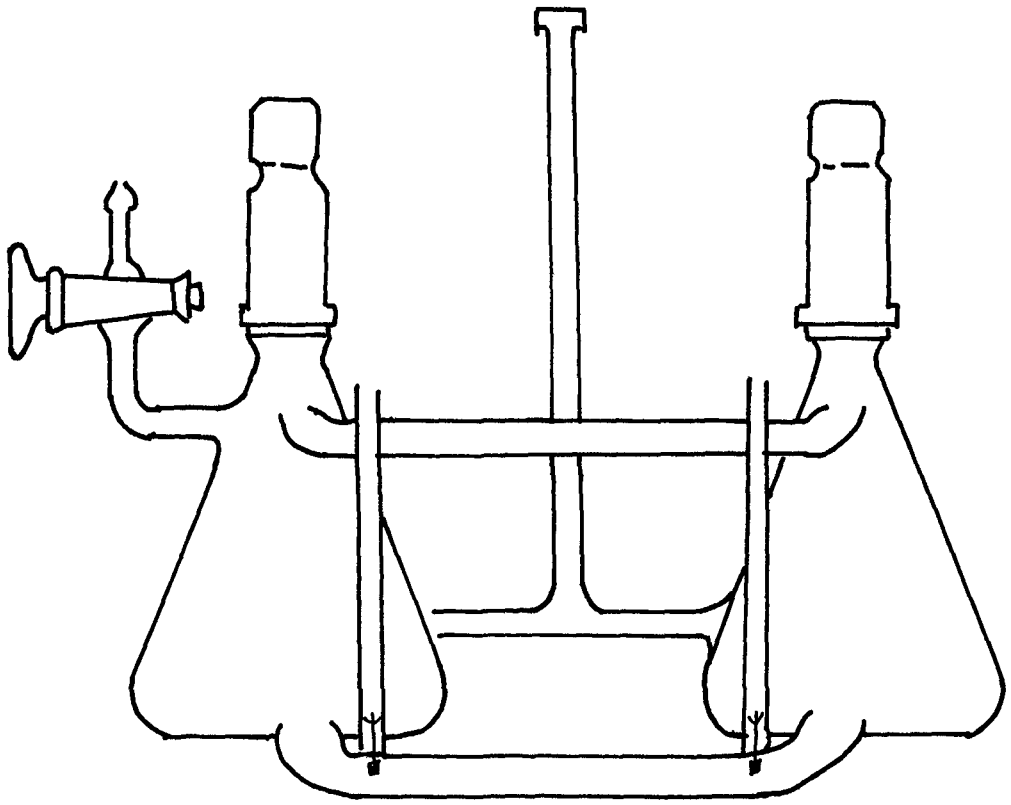
is well established[51] and therefore, the cell was calibrated using this secondary standard. The cell constant is given by the equation

$$G = 0.010433 \times R \qquad (15)$$

where R is the observed minimum resistance of the H_2O-SO_3 system.

The Apparatus and Experimental Techniques: The cell used in the present work is essentially the same as designed by Solomons[52] Figure-1 shows a typical conductivity cell which consists of a tube approximately 12 cm. long and having outside diameter 1 cm, containing the electrodes and joining two 125 ml. conical flasks. The electrodes were made from platinum foil and firmly fixed on the tube so that no displacement could occur. The conical flasks were fitted with a socket (B19 standard joint) and were capped (B19 standard joint) to exclude all moisture from the cell.

Preparation of electrodes: The electrodes were covered with a layer of platinum black in order to eliminate electrode polarization resistance.[53] The platinising solution used was that recommended by Jones and Bollinger[54] and consisted of a 0.03% solution of chloroplatinic acid with 0.025% lead acetate and 0.025N hydrochloric acid. Platinum



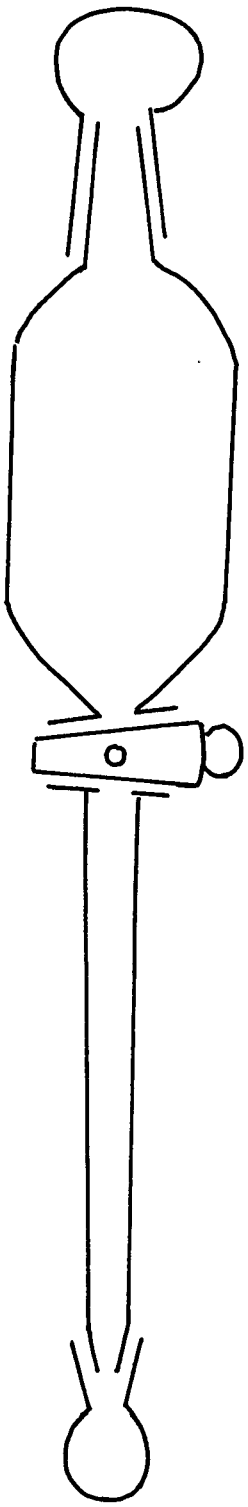
CONDUCTIVITY CELL

Fig.1

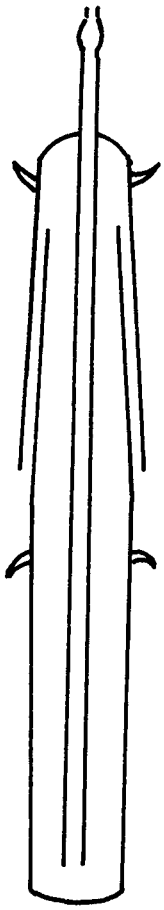
black was deposited on the electrodes by electrolysing this solution with a current of 20 milli amperes (which was reversed every thirty seconds) for about half an hour. After this heavy coating they were "greyed" by heating in hot flame and then replatinised for another ten minutes. Thus stable deposits of platinum were obtained which did not flake off. The electrodes were cleaned and replatinized frequently. They were cleaned by electrolysing a solution of aquaregia with a direct current of 20 milliamperes, reversed every thirty seconds.

Thermostat : The conductance measurements were carried out at 35 $\pm$ 0.1^{o}C in a thermostatted bath whose temperature was regulated by an automatic regulator.

General Technique: In order to make a series of electrical conductivity measurements, a weighed amount of about 50-100 gms. of chlorosulphuric acid was taken in a previously cleaned and dried cell. Small known amount of solutes were added by means of a weight-pipette or a weight burette (Figure-2) depending on whether the solute was liquid or solid. The solute was thoroughly mixed with the solvent in the cell by swirling. Care was taken to keep the caps of the conical flasks tightly closed so as not to allow the



WEIGHTBURETTE



WEIGHTPIPETTE

Fig.2

escape of any gas from cell. After this the conductivity of the solution was read from the conductivity bridge (systronic type 301-1).

Determination of γ values from conductometric measurements:

The number of moles of anion SO_3Cl^- or cation $H_2SO_3Cl^+$ of solvent self-dissociation produced by each mole of solute in chlorosulphuric acid[23] is given by the symbol γ. Its value can be readily determined from conductometric measurements in chlorosulphuric acid. It has been suggested that most of the current in the solution is carried by the SO_3Cl^- and/or $H_2SO_3Cl^+$ ions which conduct by an abnormal proton-transfer mechanism similar to that found for HSO_4^- and $H_3SO_4^+$ ions in sulphuric acid[55] and SO_3F^- and $H_2SO_3F^+$ ions in fluorosulphuric acid[56] Thus the conductivities of solutions in chlorosulphuric acid is determined almost entirely by the concentration of SO_3Cl^- and/or $H_2SO_3Cl^+$ ions present. Since it is known that potassium chloride behaves as a strong electrolyte in chlorosulphuric acid[23] producing one mole of SO_3Cl^- per mole of the solute, the γ value of a base B is, determined by comparing the concentration of the base giving a certain specific conductance with the concentration of the strong electrolyte, KCl that gives the

same specific conductance.

In Figure-3, $\gamma = \frac{OY}{OX}$

where OX is the concentration of the base and OY is the concentration of KCl which gives the same specific conductance

Spectroscopic Measurements

(a) Visible and Ultraviolet Spectroscopy: When a molecule absorbs radiation its energy increases. This increase is equal to the energy of the photons expressed by the relation

$$E = h\nu$$
$$\text{or} = hc/\lambda \qquad (16)$$

where h is Planck's constant ν and λ are the frequency and wavelength of the radiation respectively and C is the velocity of light. The change may be in the electronic, vibrational or rotational energy of the molecule. Changes in electronic energy involve relatively large quanta whereas the changes in vibrational energy involve

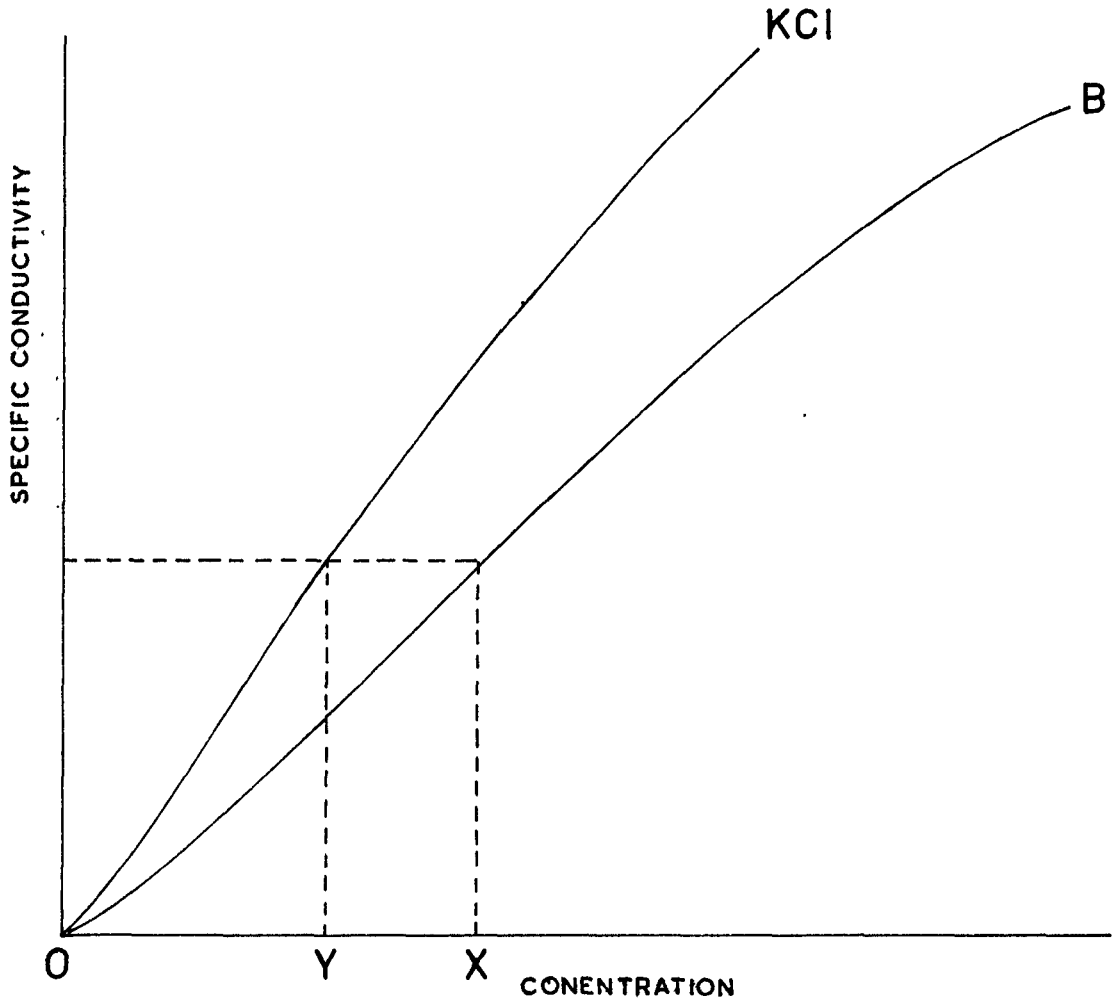


Fig.3

small quantities of energy. Rotational energy changes however, involve even smaller quanta than those required for vibrational energy changes.

When a molecule absorbs radiation of energy in the ultraviolet region changes in the electronic, vibrational and rotational energies take place simultaneously. Consequently the ultra-violet spectra of polyatomic molecules even in the gaseous state appear only as broad absorption band or band envelopes. However, in some simple molecules the fine structure has been recorded using spectrometers of high resolution. The loss of vibrational and rotational structure becomes more prominent in the spectra of liquids and of solutions because of the interaction between neighbouring molecules and by solvation.

The most helpful rule in understanding the structure of electronic transitions is the principle first putforth by Frank and later placed on a firmer theoretical basis by Condon. The Frank-Condon Principle is based upon the assumption that during an electronic transition the nuclei do not change their positions or their momenta. Consideration of the relative velocities of electrons and nuclei or the low frequencies of vibrational motions compared to the Bohr orbital frequencies of electrons, strongly suggests the plausibility of the assumption and validity of the principle has been demonstrated by application to many observed spectra.

The absroption of radiation by organic compounds in visible and ultraviolet region involves promotion of electrons in σ, π and n orbitals from the ground state to higher energy states. These higher energy states are known as antibonding orbitals. Duncan and Mateen have discussed such transitions in detail[57] and have classified them into three categories. In the first category there are N→V transitions which are from the bonding orbital in the ground state of a molecule to a higher energy antibonding orbital. For π systems the N→V transitions have been termed K bands. The second type of transition denoted by N→Q results from the excitation of the electron in a non-bonding orbital to an antibonding orbital. The N→Q transitions are usually weaker as a class than the N→V transitions. The $n\rightarrow\sigma^*$ transitions are found in the case of saturated molecules which contain singly bonded basic groups with atoms having unshared pairs of electrons (like C-OH, C-NH_2 and C-halogens). The $n\rightarrow\pi^*$ transitions are found in molecules when a hetero atom with unshared electrons is multiply bonded to another atom (like C=O and C=S). The $n\rightarrow\pi^*$ transitions are forbidden transitions and their intensities are usually very low[58] compared with the intensities of the corresponding $n\rightarrow\sigma^*$ transition. The $n\rightarrow\pi^*$ bands have also been called R bands. Lastly there

is N⟶R transition which occurs from an orbital in the ground state to one of high enough energy for the molecule ion core to resemble an atomic ion. These transitions are found in the far end of the vacuum ultra-violet region.

Most recording spectrophotometers record wavelength versus absorbance. The absorbance or "optical density" is given by

$$A = \log I_o/I$$

where I_o is the intensity of incident light and I is the intensity of transmitted light. The range of absorbance commonly recorded is 0.0-2.0. The intensity of an absorption band is calculated by the use of Lambert's and Beer's laws. These laws can be formulated by the relationship.

$$\epsilon = \frac{A}{C.l} \qquad (17)$$

where ϵ is the molar extinction coefficient, C is the molar concentration and l is the path length in centimeters. For a cell having 1 cm. path length equation(17) is transformed as

$$\epsilon = \frac{A}{C} \qquad (18)$$

Application of u-v- and visible spectroscopy in acidic media:

In u-v and visible spectroscopy we are concerned with the relatively high energy electronic excitation of molecules. Saturated molecules do not absorb in the visible and near ultra-violet region (200-800 n.m) thus excitation of σ electrons to an antibonding σ^* orbital is not normally observed. However, the absorption caused by excitation of electrons in π bonds to antibonding π^* orbital ($\pi \rightarrow \pi^*$ transition) and by excitation of nonbonded electrons to π^* orbital ($n \rightarrow \pi^*$ transition) is important in conjugated system. Steric interactions, substitution and structural changes such as ionization, tautomerism and hydrogen bonding are accompanied by changes in ultraviolet spectra.

For a long time ultraviolet and visible spectroscopy has been extensively used in the determination of the extent of ionisation of a wide variety of organic weak bases in sulphuric acid. Hammett defined a factor H_o given by the following expression:

$$H_o = pK_{BH^+} + \log \frac{B}{BH^+} \qquad (19)$$

where pK_{BH^+} is the negative logarithm of the conjugate acid BH^+ of the base B. Flexer, Hammett and Dingwall[59]

showed that spectrophotometric techniques can be applied to determine the ratio B/BH^+ from the relation-

$$\frac{BH^+}{B} = \frac{(\epsilon - \epsilon \text{ base})}{(\epsilon \text{ ion} - \epsilon)} \qquad (20)$$

where ϵ base is the extinction coefficient of the base in the solution in which it is in the basic form, ϵ ion is the value in the solution in which it is almost in the ionic form and ϵ is the value in acids of intermediate strength.

Gold and Hawes,[60] Deno and Jaruzelski[61] and Brand[62] have used this method to determine the pK_{BH^+} values of a few nitroanilines, carbinols acetophenones and aromatic nitrocompounds in sulphuric acid.

Keith Yates has in a series of papers published the pK_{BH^+} values of a few substituted amides[63,64] and acetophenones[65,66] in concentrated sulphuric acid. He has slightly modified the above method for determining BH^+/B ratio and has used the extinction coefficient value of the bases in 95% H_2SO_4 as ϵ BH^+, in 46% H_2SO_4 as ϵ B and in acid of intermediate strength as ϵ .

Recently, Gillespie and co-workers[67] on the basis of the spectrophotometric studies on solutions of a set of

aromatic nitro compounds have determined the acidity function H_o for the strong acidic media which include H_2SO_4-HSO_3F, H_2SO_4-SO_3, H_2SO_4-HSO_3Cl and H_2SO_4-$HB(HSO_4)_4$. For pure chlorosulphuric acid they found H_o value of -13.80 which is numerically 1.02 units higher than those suggested by Palm.[32]

The use of ultraviolet spectroscopy in the determination of the site of protonation in compounds in strong acidic media was first introduced by Hantzsch.[68] Later many workers[69,70] have successfully used this technique for the determination of protonation sites in acidic solutions of various compounds containing bifunctional groups.

Several other workers have used ultra-violet spectroscopy in the study of carbonium ions in strong acid solvents for example, Newman and Deno[71] showed that a third aryl group contributes little to the resonance stabilization of triaryl carbonium ions, Rosenbaum and Farrel, and their coworkers[72-75] have used this technique extensively in the study of carbonium ions.

Experimental techniques: Solutions of the compounds in alcohol as well as in chlorosulphuric acid were prepared by dissolving an analytically weighed sample. The spectra was thus recorded in a stoppered quartz cell of 1 cm. path length with a Beckman Model DK2A Ratio recording spectrophotometer at room temperature (25°C).

(b) Nuclear Magnetic Resonance Spectroscopy: The nuclei of certain isotopes possess a mechanical spin or angular momentum. The total angular momentum depends on the nuclear spin or spin quantum number I which may have values of $0, \frac{1}{2}, \frac{3}{2}$ .... (depending on the particular nucleus). The n.m.r. spectroscopy is most often concerned with nuclei having $I = \frac{1}{2}$, examples of which include $^{1}H, ^{31}P$ and ^{19}F.

For a nucleus with $I = \frac{1}{2}$ there are two values for the nuclear spin angular momentum quantum number m_I viz. $+\frac{1}{2}$ and $-\frac{1}{2}$ which in the absence of a magnetic field are degenerate. In the presence of the magnetic field however, this degeneracy is destroyed such that the positive value of m_I corresponds to the lower energy state and the negative value to higher, separated by ΔE. A nucleus with a magnetic moment can be visulised as a bar magnet which spins on its axis. The magnetic moment interacts with the external field when the nucleus is placed in it and produces a torque. This torque interacts with the angular momentum and causes magnetic moment to precess about the applied field vector, H_o. The angular frequency ω, of the precession is referred to as Larmor frequency whose magnitude is determined by the expression given below

$$\omega = \gamma H_o \qquad (21)$$

Then quantity γ (radians gauss^{-1}Sec^{-1}) referred to as the magnetogyric ratio, is a constant for a given nucleus.

In an n.m.r experiment one applies a strong homogeneous magnetic field causing the nuclei to precess. Radiation of energy comparable to $\triangle E$ is then imposed with a radio frequency transmitter. When the applied frequency from the radio transmitter is equal to the Larmor frequency the two are said to be in "resonance" and energy can be transferred to and from the source and the sample and n.m.r signals is obtained when a nucleus is excited from the low energy to the high energy state. The Larmor frequency is generally matched with a fixed radio frequency by varying the field strength H_o.

The magnitude of the field seen at the nucleus; H_N is different from the applied field H_o due to shielding by electrons and is given by the relation

$$H_N = H_o (1-\sigma) \qquad (22)$$

Where σ is a constant representing the shielding of the nucleus by the electrons. An accurate measurement of H_N and H_o is very difficult. Instead a reference material is employed and the difference in the field strengths H_S at which the sample nucleus absorbs and H_R at which the nucleus

in the reference compound absorbs is measured. The chemical shift δ which is independent of the field strength is defined as

$$\delta = \frac{H_S - H_R}{H_R} \qquad (23)$$

Since spectra are generally calibrated in cycles per sec. (c.p.s) the equation (23) may be rewritten as

$$\delta = \frac{\Delta\nu \times 10^6}{\text{fixed frequency of the probe}} \qquad (24)$$

Where $\Delta\nu$ is the difference in the absorption frequencies of the sample and reference in c.p.s., the fixed frequency or the oscillator frequency is characteristic of the instrument. A 60 Mc instrument has an oscillator frequency of 60×10^6 c.p.s. The factor δ is a dimensionless quantity expressed in parts per million (p.p.m).

The fine structure of the n.m.r. peaks due to various nuclei arises from the phenomenon known as spin-spin splitting. The separation J (usually expressed in cycles per second) between the peaks comprising the fine structure is referred to as the spin-spin coupling constant. The number of peaks in the fine structure of the spectrum due to

an atom A being split by a non-equivalent atom B is given by the following formula:

$$n = 2 \sum S_B + 1 \qquad (25)$$

Where $\sum S_B$ is the sum of the spins of equivalent B nuclei. The relative intensities of the peaks can be obtained from the coefficients of the terms that result from the binomial expansion $(1 + x)^m$, where $m = n-1$.

The spin-spin splitting pattern and characteristic J values provide extremely useful information regarding the structure of the species being investigated.

Application of NMR Spectroscopy in studies in strong acidic media: Nuclear magnetic resonance spectroscopy is a powerful tool for the study of the molecular environment of a particular nucleus. Difference in the resonance arise because of a difference in the extent of shielding of the nuclei which is influenced by, for example, the state of hybridisation and the electronegativity of the groups attached to the atom containing the nucleus.

In the study of the carbonium ions it is useful to compare their n.m.r. spectra with those of the precursor molecules. Since in the positively charged carbonium ions

the protons are expected to be less shielded than in the neutral molecules, shifts to lower fields are generally expected. Proton n.m.r. spectroscopy has been used extensively in the study of the formation of carbonium ions in strong acidic media.[76-90] Recently Olah and coworkers[91,92] have also used ^{13}C n.m.r. spectroscopy to elucidate the structure of various carbonium ions formed in the acidic media.

It has also been found helpful in the study of the determination of the protonation sites in various compounds specially those containing bifunctional group[34,35,93] viz. amides, ureas and their thio-analogues. Recently Gillespie and Birchall have pointed out that the site of protonation could be determined unambiguously if the rate of exchange of the captured proton with the solvent could be sufficiently slowed down so that a separate signal for this proton could be observed in the spectrum. They have for the first time observed[94-96] the separate peak for the conjugate acid proton i.e. $C{=}OH^+$ and $C{=}SH^+$ for amides and thio-amides at about 10.0δ and 5.0δ respectively in HSO_3F and SbF_5- HSO_3F at very low temperature.

Experimental techniques: The n.m.r. spectra of about 10% solution of compounds in chlorosulphuric acid and $CDCl_3$ were recorded on a Varian A60D. Spectrometer using

tetramethyl silane as external reference filled in a sealed capillary tube.

(c) Infrared Spectroscopy: The infrared absorption spectra of molecules result from transitions between vibrational and rotational energy levels. The infrared region of the electromagnetic spectrum covers a wide range of wavelengths from 0.8 micron to 200 micron(12,500 to 50 $cm.^{-1}$). It has been further subdivided into three regions: the near infrared region between 12500 and 4000 $cm.^{-1}$, the medium infrared region from 4000 to 650 cm^{-1} and the far infra-red region extending from 650 to about 50 $cm.^{-1}$

The infrared frequencies are determined mainly by the mechanical motions in the molecule. Vibrational transitions without rotation may be discussed in terms of the harmonic oscillator model. In the harmonic oscillator model, the restoring force is proportional to the first power of displacement (Hook's law) and the potential energy function is proportional to the square of the displacement. This model can account for fundamental vibrations occurring between the nonvibrating state and the next vibrationally excited state. In a simple diatomic molecule (X-Y), the only vibration which can occur is the periodic stretching along the X-Y bond. The stretching vibration may be

visualized as an oscillation of the two bodies X and Y connected by a spring and Hook's law is applicable to a first approximation. The vibrational energy of a diatomic molecule is given by

$$E_{vib} = \frac{h}{2\pi}\sqrt{\frac{K}{\mu}}\,(n+\tfrac{1}{2}), \quad n = 0,1,\cdots \qquad (26)$$

where h is the Planck's constant, n the vibrational quantum number, K the force constant of the bond and μ the reduced mass of the molecule defined by

$$\mu = m_x \cdot m_y / m_x + m_y$$

where m_x and m_y are atomic masses of X and Y. The energy change ΔE_{vib} for the absorption process, n = 0 to n = 1 is

$$\Delta E_{vib} = \frac{h}{2\pi}\sqrt{\frac{K}{\mu}} \qquad (27)$$

since $\Delta E_{vib} = h\nu$

or $= hc\bar{\nu}$

where ν and $\bar{\nu}$ are the vibration frequency in sec^{-1} and $cm.^{-1}$ respectively.

It, therefore, follows that the vibrational frequency in $cm.^{-1}$ is given by

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \qquad (28)$$

The value of K is of the order of 5×10^5 dynes $cm.^{-1}$ for single bonds and is about twice and three times this value for double and triple bonds respectively.

A non-linear molecule of n atoms has 3n degrees of freedom which are described as three rotational and three transitional and 3n-6 vibrational motions. A non-linear molecule should then show 3n-6 different strong i,r. absorptions. In certain molecules however, one observes a lesser number of normal vibrational frequencies than expected in the infrared spectra. This is due to some selection rules which should be followed by the normal modes of vibration of the molecule. The absorption of electromagnetic radiation is possible only when there is a change in the dipole moment of the molecule during the normal vibration. The intensity of the resulting absorption band is proportional to the square of the change in dipole moment. When there is no change in the dipole moment of a molecule during a normal vibration it will be infrared inactive.

It has been found that some of the vibrational frequencies are associated with specific groups of atoms and are the same irrespective of the molecule in which this group is present. These are called characteristic frequencies

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and their constancy results from the constancy of bond force constants from molecule to molecule. The important observation that the infrared spectrum of a complex molecule consists of a number of characteristic group frequencies makes infrared spectroscopy an unique and powerful tool in structural analysis. The vibrations associated with covalently linked atoms may be classified into "stretching" vibrations involving periodic extensions and contractions of the bonds and "bending or deformation" vibrations involving periodic bending of bonds. Bending force constants are generally about an order of magnitude smaller than the stretching force constants and are more sensitive to the environment. Variations in the environment give rise to small changes in the characteristic frequency of a group. The characteristic group frequencies relevant to the present work only have been described in the following few lines.

All the carboxylic acid anhydrides show two absorption bands in the region 1870-1740 $cm.^{-1}$ The position of the bands depend on the ring size of the anhydride as well as on the presence of the conjugated unsaturation. For example,[97] in acetic anhydride the bands are at 1824 cm^{-1} and 1748 cm^{-1}, in succinic anhydride at 1865 cm^{-1} and 1782 cm^{-1} and in phthalic anhydride at 1845 cm^{-1} and 1775 $cm.^{-1}$ The doubling of the carbonyl frequencies in anhydrides has been explained[97]

to be due to the coupling of the two equal C=O frequencies which leads to resonance splitting. In addition to the carbonyl absorptions the anhydrides also show strong C-O-C stretching vibrations occurring[98] in the region 1175-1045cm.$^{-1}$ for open chain and 1310-1210 cm.$^{-1}$ for cyclic compounds. Protonation at carbonyl oxygen atom should cause a shift of this band to lower frequency. Similarly protonation at ethereal oxygen atom would also cause a shift of C-O-C band to lower frequency.

Benzene ring shows four diagnostic bands in 1650-1450 cm.$^{-1}$ It is well established that these bands are due to C=C skeletal in-plane vibrations. It has been shown[98] that the positions and intensities of these bands are dependent on the type of substitution and the nature of substituents.

Application of Infrared Spectroscopy in strong acidic media:

From the infrared spectroscopic studies a strong evidence for the formation of the various organic and inorganic cationic species in acidic media has been obtained. The appearance of a band at 2160 cm^{-1} in solution of N_2O_3 and at 2320 cm^{-1} in solution of N_2O_5 in disulphuric acid[46] has been ascribed to the formation of cationic species NO^+ in the former case and NO_2^+ in the latter. Formation of the

cationic species $SeCl_3^+$ and PCl_4^+ in solutions of selenium tetrachloride[26] and phosphorous pentachloride[99] in fluorosulphuric acid have been indicated from the i.r. spectral studies. Gillespie and coworker[100] have suggested that the characteristic stretching vibration of the $C \equiv O^+$ group in the acyl ions occur at about 2200 $cm.^{-1}$ whereas for the protonated carbonyl group the characteristic stretching vibration has been shown[101-103] to occur at about 1600 $cm.^{-1}$

Experimental Technique: It has been shown that AgCl prism can be used as window material for studies in the strong acidic solutions.[100] Thin polyethylene and teflon sheets have also been successfully used by some workers.[46,101] In the present studies i.r. spectra of solutions of organic acid anhydrides have been recorded on a Perkin Elmer 337 spectrophotometer at room temperature (25°C). Envelope cells were made from two thin polyethylene sheets. One or two drops of the concentrated solutions of the compounds in HSO_3Cl were pressed into homogeneous thin film and the cell was then sealed off. The spectra were not very well defined due to a high background absorption of the acid and polyethylene. However, they were transparent in the region 1500-2200 $cm.^{-1}$ to enable the study of changes in the carbonyl stretching frequencies.

CHAPTER - III

BEHAVIOUR OF UREAS AND THIOUREAS IN CHLOROSULPHURIC ACID

INTRODUCTION

There has been during the last two decades considerable discussion regarding the structure of protonated amides and ureas and their thio analogues both in the solid state as well as in solutions. Thus, while attempts have been made to elucidate the structure of their solid hydrochlorides and nitrates with the help of u.v., i.r. spectroscopic[33,104] and x-ray studies;[105] several reports have also appeared during recent years regarding the mode and extent of protonation of such compounds in acidic solutions.[34,35] Studies have been carried out in aqueous sulphuric acid of varying strengths and in the lesser basic anhydrous media fluorosulphuric acid and SbF_5-HSO_3F mixture. Liler has recently proposed on the basis of n.m.r. spectroscopic studies on a few substituted amides in aqueous sulphuric acid[36,37] and on acetamide and N^{15}-acetamide in fluorosulphuric acid;[38] that while in dilute aqueous acids N-protonated species are formed in the anhydrous acid solutions, O-protonated species are predominant. Thus the question of the site of protonation in such compounds seemed for a while to have been settled by Liler's work but very recently several

authors[39-42] have raised serious doubts about N-protonation even in dilute aqueous acids. The behaviour in strong acids of ureas, and thioureas have not been as much explored as that of amides and thioamides. However, Gillespie and Birchall on the basis of the n.m.r. studies[95] of solutions of urea, 1,3-dimethylurea, thiourea and N-methylthiourea in fluorosulphuric acid suggested an incomplete protonation on nitrogen atom alongwith a complete monoprotonation on sulphur atom of the thiocarbonyl group in thioureas. They did not however, get any conclusive evidence regarding the site of protonation in urea and 1,3-dimethylurea.

As no such studies have been reported in chlorosulphuric acid which is intermediate in strength between sulphuric acid and fluorosulphuric acid it was thought worthwhile to examine the behaviour of urea, 1,3-dimethylurea, 1,3-diphenylurea, tetramethylurea, 1,3-di-1-naphthylurea, cyanoacetylurea, biurea, thiourea, N-allylthiourea, N,N'-diallylthiourea, N,N'-diisopropylthiourea, 1,3-diphenylthiourea and 2,5-dithiobiurea in chlorosulphuric acid with a view to determining the site and extent of protonation in these compounds.

PREPARATION AND PURIFICATION OF REAGENTS

Purification of reagents:

Urea and 1,3-diphenylurea (B.D.H., England) were recrystallised from alcohol and dried in air. These melted sharply at 133°C and 240°C respectively.

Thiourea and 1,3-diphenylthiourea (B.D.H.,England) were recrystallised from alcohol and dried in air. These melted sharply at 182°C and 154°C respectively.

1,3-dimethylurea m.p. 107°C, 1,3-di-1-naphthylurea m.p. 297°C, 2,5-dithiobiurea m.p. 192°C, N-allylthiourea m.p.78°C, N,N'-diallylthiourea m.p. 46°C, biurea m.p.250°C decomposed (all Eastman Kodak reagents) N,N'-diisopropylthiourea m.p. 151°C (Fluka, A.G), cyanoacetylurea m.p.207°C (Koch Light) and tetramethylurea (E.Merck) were used as received.

TABLE - 2

Specific conductance of solutions of potassium chloride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 118.5260 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1697
0.1041	0.1917
0.4765	0.2458
0.7908	0.3105
0.9304	0.3495
1.6490	0.5033
2.0370	0.5784
2.5950	0.6839

EXPERIMENT - 2: 100.5456 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1657
0.0450	0.1803
0.2466	0.2205
0.5091	0.2716
0.8200	0.3323
0.9986	0.3835
1.3020	0.4314
2.1950	0.5882
2.4650	0.6520

LiCl

TABLE - 3

Specific conductance of solutions of urea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 70.0254 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$K_s 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1717
0.0552	0.1750
0.2250	0.2103
0.5515	0.2805
0.8015	0.3255
1.3250	0.4314
2.3670	0.6413
2.5050	0.6650

EXPERIMENT - 2: 95.5920 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$K_s 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1697
0.1498	0.1895
0.2948	0.2356
0.4660	0.2756
0.7431	0.3195
0.8986	0.3795
1.5040	0.4913
2.0150	0.5784
2.5670	0.6661

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TABLE - 4

Specific conductance of solutions of 1,3-dimethylurea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 106.0502 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1717
0.0856	0.2077
0.3328	0.2556
0.6901	0.3295
1.0720	0.4245
1.4350	0.4964
1.9540	0.5952
2.4140	0.6961
2.9560	0.8030

EXPERIMENT - 2: 100.5432 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1717
0.2387	0.2396
0.4714	0.2996
0.8997	0.3895
1.3330	0.4804
1.6930	0.5523
2.1860	0.6482
2.6750	0.7520
2.8950	0.7805

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TABLE - 5

Specific conductance of solutions of 1,3-diphenylurea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 81.0526 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	K x 10^2 ohm^{-1}cm^{-1}
0.0000	0.1697
0.0575	0.1757
0.2353	0.2077
0.4931	0.2566
0.9621	0.3565
1.5330	0.4484
2.0150	0.5452
2.3560	0.6102
2.6540	0.6556

EXPERIMENT - 2: 85.2240 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	K x 10^2 ohm^{-1}cm^{-1}
0.0000	0.1707
0.1214	0.1887
0.3730	0.2317
0.7431	0.3045
1.3200	0.4114
1.7750	0.5013
2.2550	0.5802
2.8030	0.6851

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TABLE - 6

Specific conductance of solutions of 1,3-di-1-naphthylurea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 115.5002 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1717
0.0454	0.1767
0.2428	0.2246
0.5293	0.2606
0.9273	0.3355
1.2150	0.3954
1.4990	0.4433
1.8330	0.5052
2.2530	0.5853

EXPERIMENT - 2: 80.0550 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1715
0.1385	0.1917
0.3856	0.2286
0.7695	0.3052
1.0860	0.3654
1.3430	0.4214
1.6680	0.4783
1.9470	0.5342
2.5070	0.6352

TABLE - 7

Specific conductance of solutions of tetramethylurea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 86.6620 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1697
0.2023	0.2312
0.4248	0.2896
0.7426	0.3708
1.1280	0.4801
1.2760	0.5251
1.2750	0.5745
1.7550	0.6498
2.0560	0.7248

EXPERIMENT - 2: 61.6956 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1700
0.1195	0.2050
0.2756	0.2498
0.5765	0.3351
0.9256	0.4248
1.2080	0.4995
1.3780	0.5505
1.6550	0.6251
1.9520	0.6998
2.1750	0.7495

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TABLE - 8

Specific conductance of solutions of thiourea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 100.9522 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1707
0.2130	0.2237
0.5396	0.2876
0.8830	0.3515
1.3860	0.4506
1.8750	0.5513
2.2530	0.6232
2.7390	0.7191

EXPERIMENT - 2: 99.9560 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1707
0.0551	0.1800
0.1350	0.2102
0.5052	0.2651
0.7499	0.3016
1.0190	0.3595
1.5560	0.4765
2.2240	0.6204
2.6390	0.7058

TABLE - 9

Specific conductance of solutions of 1,3-diphenylthiourea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 88.5501 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K_s 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1677
0.0537	0.1757
0.2954	0.2237
0.5949	0.2716
0.9941	0.3515
1.2310	0.3995
1.6580	0.4793
2.3670	0.6152

EXPERIMENT - 2: 69.9522 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K_s 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1697
0.1681	0.1997
0.4569	0.2556
0.7522	0.3036
1.1100	0.3755
1.4550	0.4394
1.9770	0.5353
2.2650	0.5905

TABLE - 10

Specific conductence of solutions of N,N'-diisopropylthiourea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 116.5520 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\chi \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1707
0.2028	0.2227
0.4843	0.2916
0.7906	0.3605
1.0850	0.4095
1.5040	0.5003
1.7520	0.5552
2.2500	0.6507

EXPERIMENT - 2: 100.1660 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\chi \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1717
0.0612	0.1837
0.3758	0.2656
0.6412	0.3216
0.9675	0.3995
1.3020	0.4624
1.6360	0.5353
1.9750	0.6005
2.3750	0.7205

TABLE - 11

Specific conductance of solutions of N-allylthioures in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 111.9560 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1687
0.0324	0.1757
0.2791	0.2396
0.5055	0.2712
0.6336	0.3005
0.9614	0.3635
1.4360	0.4743
1.6270	0.5013

EXPERIMENT - 2: 55.5112 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1677
0.1343	0.2077
0.4546	0.2566
0.7686	0.3435
1.0250	0.3755
1.1830	0.4235
1.5550	0.4820
1.7620	0.5263
1.6750	0.5456

TABLE - 12

Specific conductance of solutions of N,N'-diallylthiourea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 98.0050 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1} cm^{-1}
0.0000	0.1677
0.2267	0.2218
0.5258	0.2855
0.9072	0.3505
1.3560	0.4305
1.5050	0.4750
1.9950	0.5361
2.7320	0.6603

EXPERIMENT - 2: 90.5060 gm of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1} cm^{-1}
0.0000	0.1697
0.1622	0.2017
0.3295	0.2523
0.6958	0.2946
1.2010	0.4172
1.4910	0.4614
1.8040	0.5256
2.3960	0.6232
3.0270	0.7075

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TABLE - 13

Specific conductance of solutions of biurea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 85.0506 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1712
0.0891	0.2317
0.3207	0.2956
0.4968	0.3483
0.6785	0.4634
1.2080	0.5592
1.6010	0.6791
1.8250	0.7358

EXPERIMENT - 2: 90.9510 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1712
0.0257	0.1997
0.2296	0.2716
0.3642	0.3116
0.7045	0.4154
1.0040	0.5033
1.2550	0.5761
1.5560	0.6395
1.7520	0.7153

TABLE - 14

Specific conductance of solutions of cyanoacetylurea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 108.8502 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1697
0.2266	0.2576
0.4962	0.3375
0.8570	0.4654
1.1340	0.5612
1.2350	0.6250
1.3590	0.6412
1.5390	0.7051

EXPERIMENT - 2: 60.5028 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1685
0.3053	0.2736
0.5685	0.3749
0.6919	0.4094
1.0330	0.5373
1.2850	0.6172
1.3500	0.6258
1.4840	0.6811
1.7580	0.7552

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TABLE - 15

Specific conductance of solutions of 2,5-dithiobiurea in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 94.5560 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1717
0.1656	0.2476
0.3821	0.3195
0.6352	0.4374
0.9263	0.5081
1.1740	0.5912
1.5040	0.7111
1.5660	0.7350

EXPERIMENT - 2: 60.6682 gm of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1707
0.1005	0.2253
0.2732	0.2676
0.5193	0.3675
0.7568	0.4474
1.0430	0.5513
1.3520	0.6551
1.5330	0.7191
1.7020	0.7830

DISCUSSION

All the ureas and thioureas readily dissolved in chlorosulphuric acid giving colourless solutions excepting N,N'-diisopropylthiourea and 1,3-di-1-naphthylurea which gave a violet and a dark-blue coloured solutions respectively. In none of the cases any evolution of hydrogen chloride gas was observed suggesting that these compounds behave as simple bases in chlorosulphuric acid and form the corresponding conjugate acid (BH^+) according to the following reactions;

$$B + HSO_3Cl \rightleftharpoons BH^+ + SO_3Cl^- \qquad (29)$$

As the conductometric measurements alone could not possibly give any conclusive information regarding the site of protonation, nuclear magnetic resonance and ultra-violet spectroscopic studies on the solutions of these compounds were undertaken. The results of these studies have been discussed in the following lines.

Conductometric Studies: The conductivities of all the bases have been compared with that of potassium chloride for determining the γ factor. The average value of γ

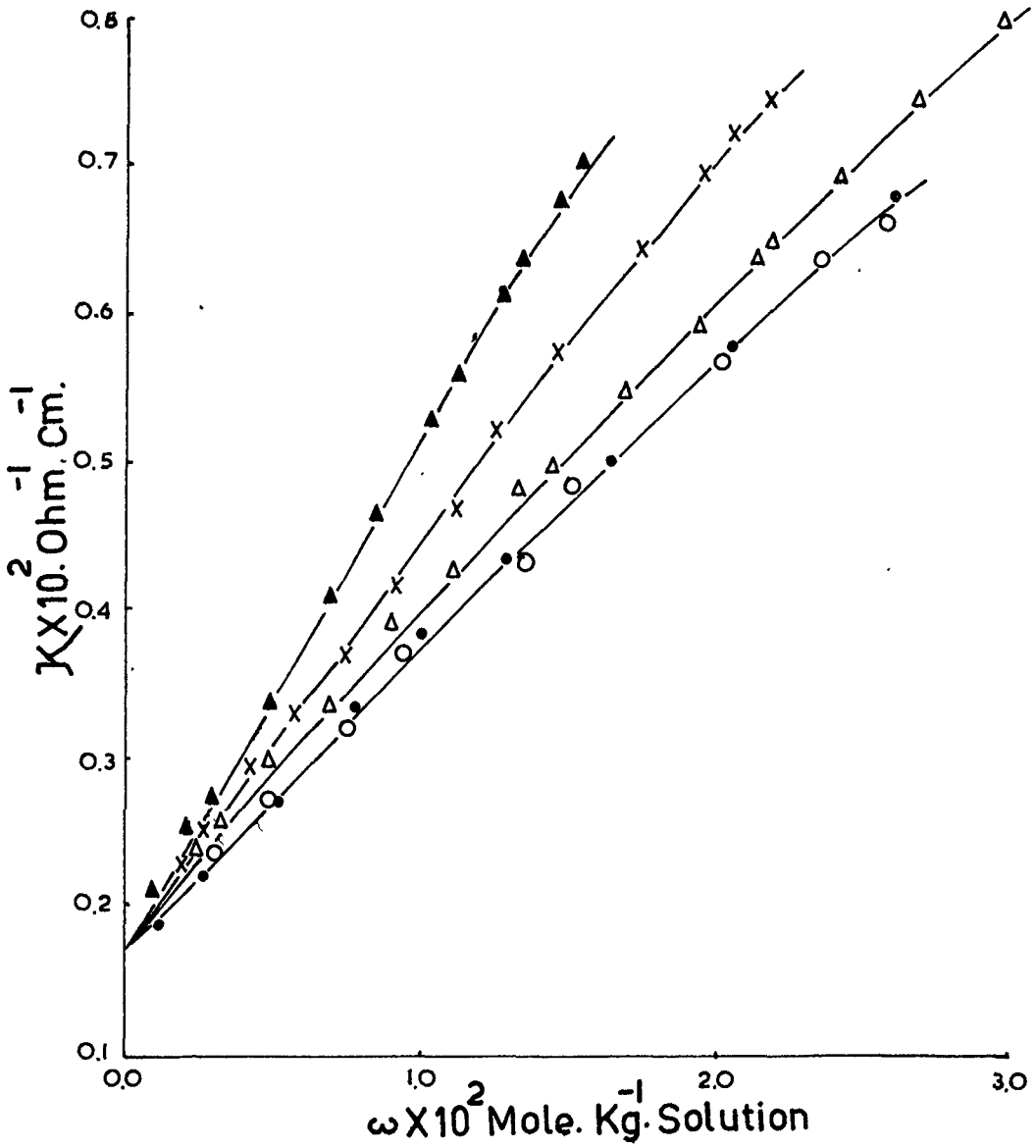
obtained within the range of concentrations studied has been shown in Table -16.

All the ureas and thioureas gave stable and conducting solutions in chlorosulphuric acid. From Figures 4 and 6 it is clear that the specific conductances of urea and thiourea are similar to that of potassium chloride solutions suggesting monoprotonation in these bases (γ = 1.00). The specific conductances of all the substituted ureas and thioureas studied have also been compared with that of their parent compounds urea and thiourea in order to gain information about the effect of substitution on the extent of protonation in these compounds. It is evident from Table -16 that the extent of protonation in tetramethylurea, 1,3-dimethylurea, and N,N'-diisopropylthiourea (γ = 1.38; 1.14, and 1.16 respectively) is greater than in urea and in thiourea. The extent of protonation in 1,3-diphenylurea, 1,3-di-1-naphthylurea and 1,3-diphenylthiourea (γ = 0.87, 0.87 and 0.88 respectively) is lower than in urea and in thiourea. This may be due to the inductive effect of the substituents on the basicity of these compounds. While the site of protonation could not be clearly indicated by conductometric studies it seems reasonable to suggest the reaction of these

TABLE - 16

Average value of γ calculated from the specific conductances of the compounds in chlorosulphuric acid at 35°C.

Compound	γ
Urea	1.00
1,3-dimethylurea	1.14
1,3-diphenylurea	0.87
1,3-di-1-naphthylurea	0.87
Tetramethylurea	1.38
Cyanoacetylurea	1.80
Biurea	1.80
Thiourea	1.00
N-allylthiourea	1.00
N,N'-diallylthiourea	1.00
N,N'-diisopropylthiourea	1.16
1,3-diphenylthiourea	0.88
2,5-dithiobiurea	1.90



- ● POTASSIUM CHLORIDE
- ○ UREA
- Δ 1,3-DIMETHYLUREA
- X TETRAMETHYLUREA
- ▲ CYANOACETYLUREA

Fig.4

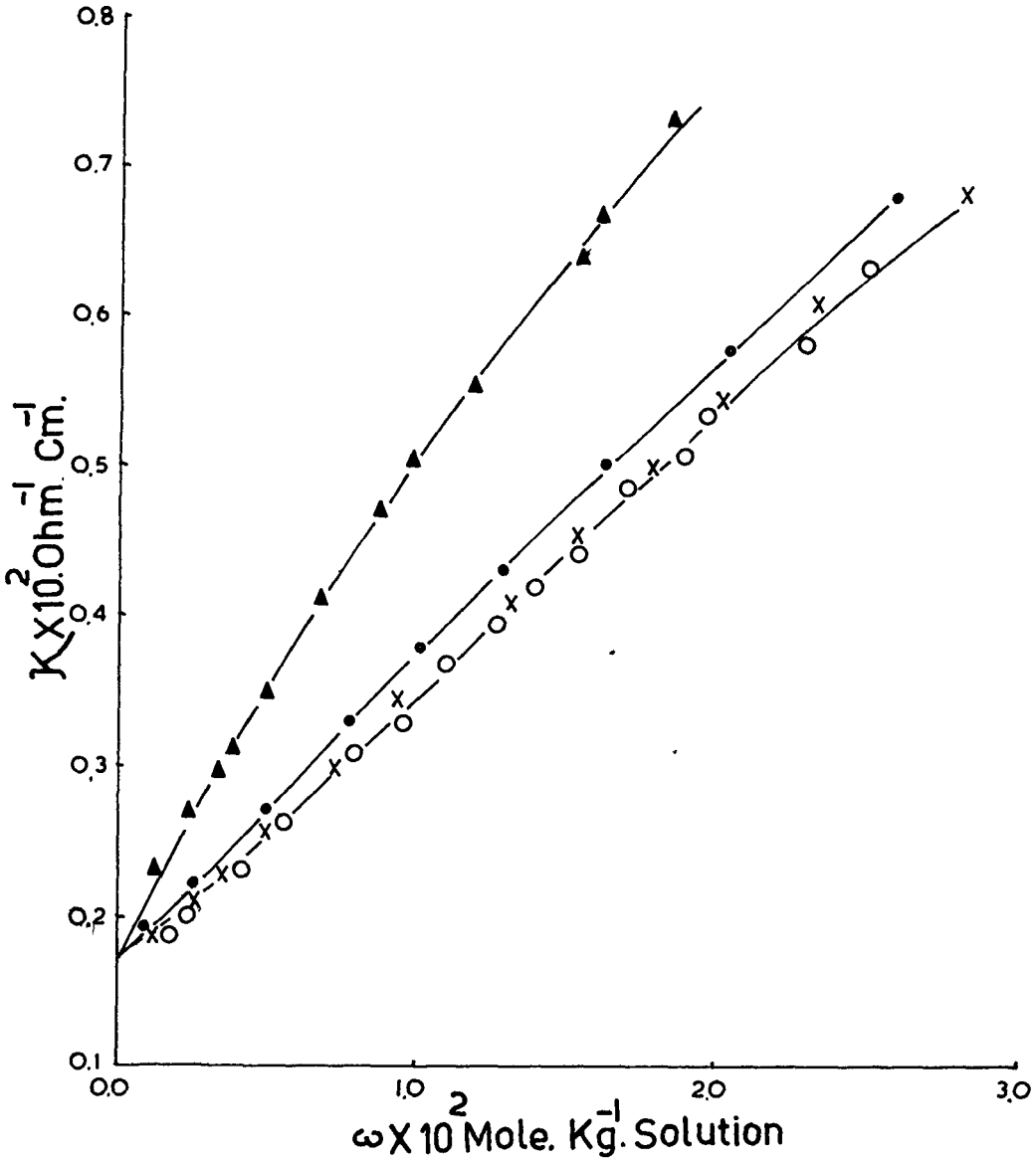
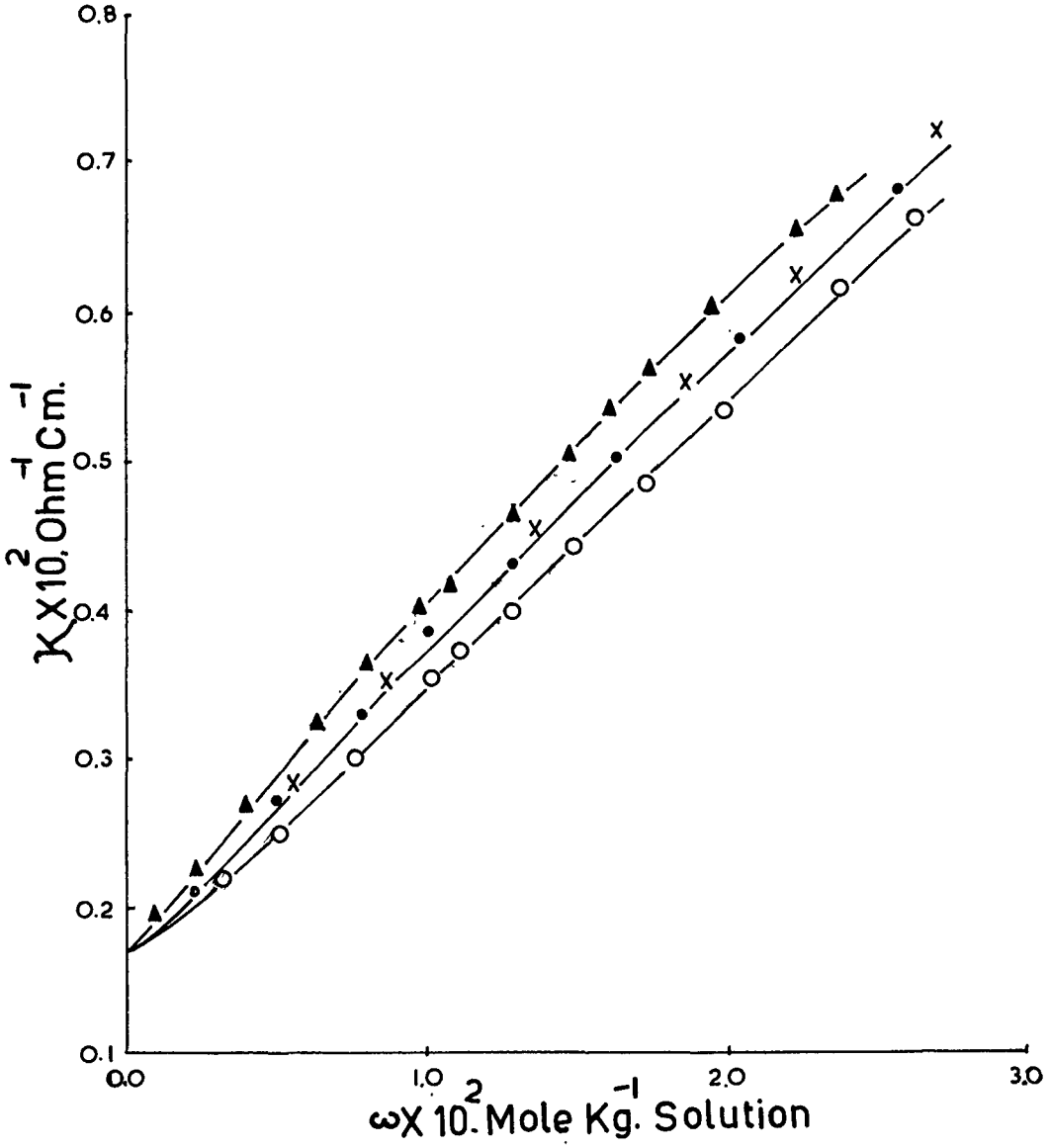
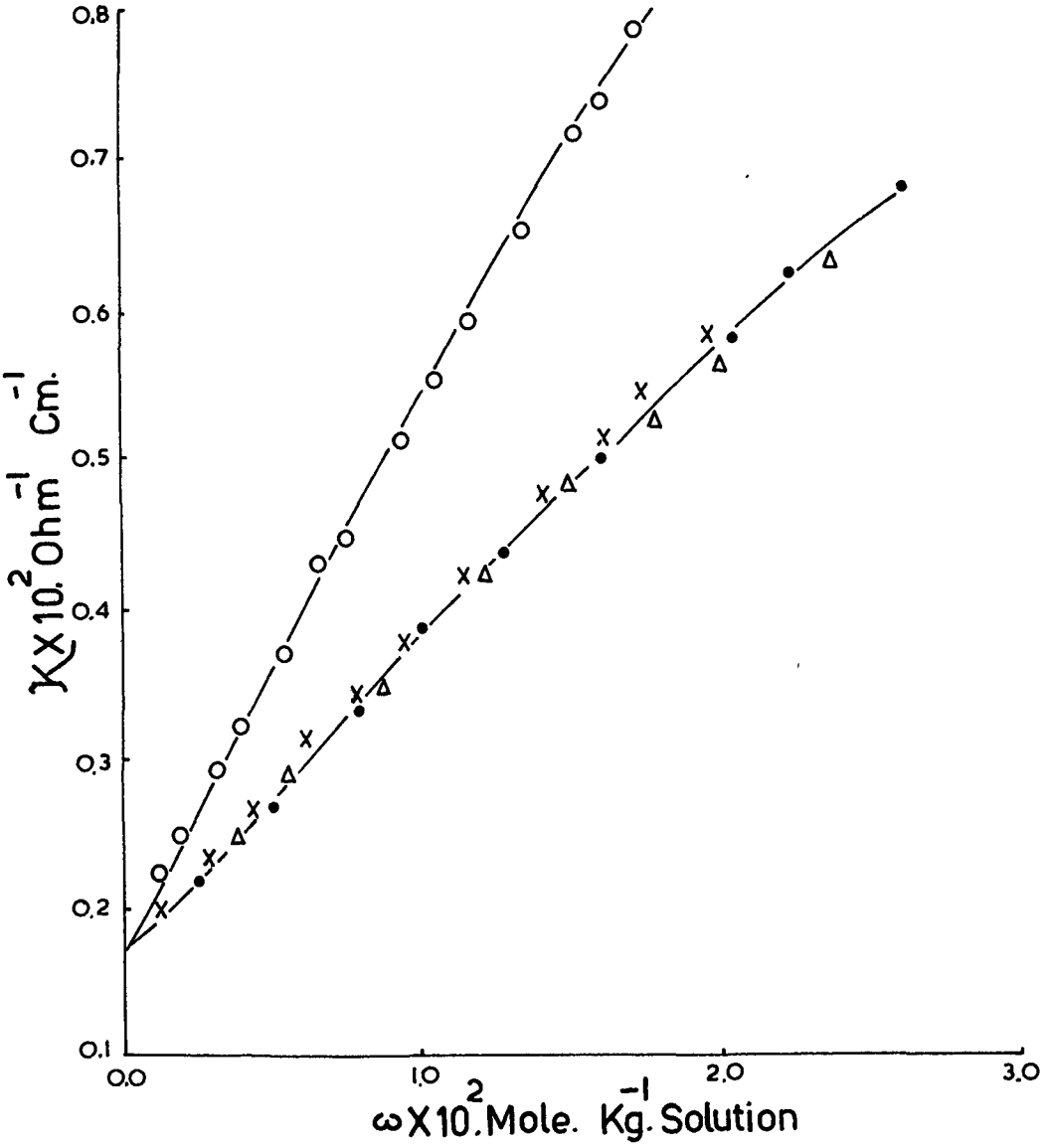

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1.0
2.0
3.0
K X 10^2 Ohm^-1 Cm^-1
ω X 10^2 Mole. Kg^-1 Solution
• POTASSIUM CHLORIDE
▲ BIUREA
O 1,3-DI-1-NAPHTHYLUREA
X 1,3-DIPHENYLUREA

Fig.5



- POTASSIUM CHLORIDE
- X THIOUREA
- ▲ N,N'—DIISOPROPYLTHIOUREA
- O 1 3-DIPHENYLTHIOUREA

Fig.6



O 2,5-DITHIOBIUREA
• POTASSIUM CHLORIDE
X N-ALLYLTHIOUREA
Δ N,N'-DIALLYLTHIOUREA

Fig. 7

compounds as typified by that of urea given below:

$$NH_2 - CO-NH_2 + HSO_3Cl \rightleftharpoons [NH_2-CO-NH_2H^+] + SO_3Cl^- \quad (30)$$

Biurea, 2,5-dithiobiurea and cyanoacetylurea gave stable and highly conducting solutions (δ = 1.80, 1.90 and 1.80 respectively) in HSO_3Cl. It appears that there is an incomplete diprotonation of these compounds. The ionization of biurea, 2,5-dithiobiurea and cyanoacetylurea in HSO_3Cl may be formulated as:

$$NH_2-CO-NH-NH-CO-NH_2 + 2HSO_3Cl \rightleftharpoons [NH_2-CO-NH-NH-CO-NH_2H_2^{++}] + 2SO_3Cl^- \quad (31)$$

$$NH_2-CS-NH-NH-CS-NH_2 + 2HSO_3Cl \rightleftharpoons [NH_2-CS-NH-NH-CS-NH_2H_2^{++}] + 2SO_3Cl^- \quad (32)$$

$$N\equiv C-CH_2-CO-NH-CO-NH_2 + 2HSO_3Cl \rightleftharpoons [N\equiv C-CH_2-CO-NH-CO-NH_2H_2^{++}] + 2SO_3Cl^- \quad (33)$$

A relative order of basicity of these compounds on the basis of the extent of protonation obtained in present studies can be written as:

A - Cyanoacetylurea $\backsim$ biurea $\rangle$ tetramethylurea $\rangle$ 1,3-dimethylurea $\rangle$ urea $\rangle$ 1,3-diphenylurea $\backsim$ 1,3-di-1-naphthylurea

B - 2,5-dithiobiurea > N,N'-diisopropylthiourea > N-allylthiourea ~ N,N'-diallylthiourea ~ thiourea > 1,3-diphenylthiourea

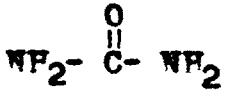
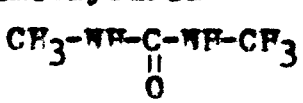
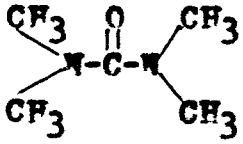
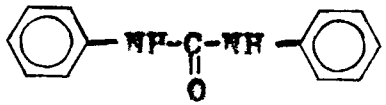
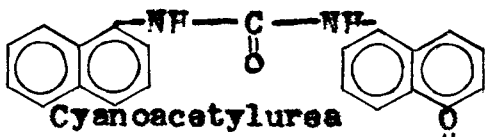
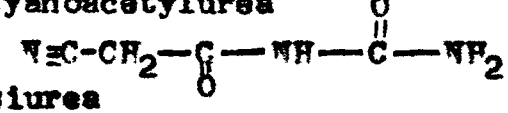
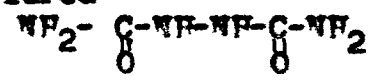
NMR Spectroscopic Studies: The results of the n.m.r. measurements on solutions of these compounds have been summarized in Tables-17 and 18.

The aqueous solution of urea shows a peak at 6.08δ attributable to the NH_2 protons.[95] However, the n.m.r. spectrum of its solution in chlorosulphuric acid showed only a broad solvent peak and no other peak similar to that observed by Gillespie and Birchall for its solution in sulphuric and fluorosulphuric acids.[95] The appearance of a broad solvent proton peak in the n.m.r. spectra of the compounds behaving as bases in strong acidic media has been suggested to be due to a rapid exchange of the proton on the conjugate acid thus formed with that of the solvent.[94] This also explains the absence of the peak attributable to the proton of the conjugate acid in such solutions.

In the case of 1,3-dimethylurea and tetramethylurea in chlorosulphuric acid only one peak was observed at 3.20δ and 2.88δ respectively and is attributed to the N-methyl protons. This peak is similar in position to that reported[95] in 1,3-dimethylurea solution in H_2SO_4 and HSO_3F at 3.33δ and 3.43δ respectively.

TABLE - 17

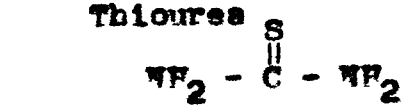
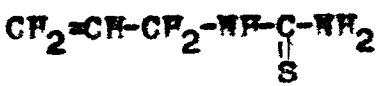
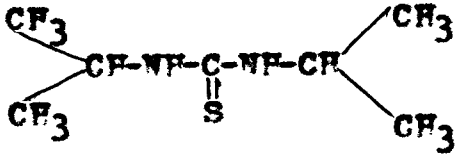
Chemical shifts in p.p.m. for compounds in chlorosulphuric acid at 25°C using T.M.S. as external reference.

Compound	Solvent peak	C-NH	$C-NH_2$	N-Ph	$N-CH_3$	$C(=O)-CH_2$
Urea 	b	-	-	-	-	-
1,3-dimethylurea 	b	-	-	-	3.20	-
Tetramethylurea 	b	-	-	-	2.88	-
1,3-diphenylurea 	b	-	-	8.25	-	-
1,3-di-1-naphthylurea 	b	-	-	8.33	-	-
Cyanoacetylurea 	b	8.66	6.25	-	-	3.33
Biurea 	b	3.33	8.60 (7.50)*	-	-	-

* = Peak observed in CF_3COOH, b = broad

TABLE - 18

Chemical shifts in p.p.m. for compounds in chlorosulphuric acid at 25°C using T.M.S.as external reference.

Compound	Solvent peak	C=SH	C-NH	$C-NH_2$	$C-CH_3$	N-CH or $N-CH_2$	CH_2= C and C=CH	N-Ph
Thiourea 	b	-	-	7.83	-	-	-	-
1,3-diphenylthiourea 	S	5.23 S	9.28	-	-	-	-	8.33
N-allylthiourea 	b	2.50 b	5.66	7.83	-	1.83	4.16,4.88	-
N,N'-diisopropylthiourea 	b	3.26 S	-	-	1.83	4.08	-	-
2,5-dithiobiurea 	b	-	10.30	8.50	-	-	-	-

b = broad S = Sharp

Solutions of 1,3-diphenylurea and 1,3-di-1-naphthylurea in HSO_3Cl gave peaks only due to benzene ring protons centered at 8.25δ and 8.33δ respectively with a broad solvent peak. In none of the above mentioned ureas the conjugate acid proton peak or any peak due to hydrogen directly attached to the unaffected nitrogen atom was observed. Low temperature n.m.r. studies of these compounds might reveal a separate peak for the corresponding conjugate acid proton. It is however, noteworthy that Gillespie and Birchall did not observe any peak for the conjugate acid of urea and 1,3-dimethylurea in HSO_3F and SbF_5-HSO_3F mixture even at as low a temperature as -80°C. It is thus clear that the n.m.r. spectra of these compounds in any of the solvents mentioned above did not prove to be of much help in gaining any clue as to the site of protonation.

In the n.m.r. spectrum of biurea in trifluoroacetic acid a single broad peak was observed at 7.50δ . This broad peak could be due either to the NH or NH_2 protons and can not be unambiguously assigned. However, it is tentatively assigned to the NH_2 protons. The spectrum of this compound in HSO_3Cl contained two peaks of relative area 1:2 attributable to the unaffected NH and NH_2 protons respectively. This at least shows that protonation is not

occurring on any of these two nitrogen atoms and must therefore, be occurring at the oxygen atoms of the carbonyl group. However, due to its exchange with the solvent proton the $C=\overset{+}{O}H$ proton could not be observed as evidenced by the appearance of a broad solvent peak in the spectrum.

The conductivity results of the cyanoacetylurea in chlorosulphuric acid (Table -16) indicate diprotonation and its n.m.r spectrum shows peaks at 3.33δ, 6.25δ and 8.66δ attributable to the CH_2 and the unaffected NH_2 and NH protons respectively alongwith a broad solvent peak. Clearly the only remaining sites susceptible for protonation are the two oxygen atoms and it is here that the protonation must be occurring.

The behaviour of thiourea in chlorosulphuric acid is found to be entirely different from that in sulphuric and fluorosulphuric acids. Thus while in sulphuric and fluorosulphuric acids only one peak at about 5.00δ attributable to $C=SH^+$ proton has been observed and a partial protonation at nitrogen atom alongwith a complete protonation at sulphur atom has been proposed;[95] it is interesting to note that in chlorosulphuric acid only one peak at 7.83δ which is not shifted from its position in water and trifluoroacetic acid is observed (Table-18) alongwith a broad

solvent peak. This peak is attributed to the unaffected NH_2 protons. It is, therefore, suggested that in thiourea only monoprotonation occurs on the sulphur atom which is also consistent with the conductometric results (γ = 1.00).

In the case of 1,3-diphenylthiourea peaks attributable to benzene ring protons centered at 8.33δ, unaffected NH protons at 9.28δ and a sharp peak at 5.23δ attributable to the proton on sulphur atom (i.e. $C=\overset{+}{S}H$) with relative areas 10.00:2.04:0.88 respectively have been observed providing a clear cut evidence for the protonation on the sulphur atom only. The sharp $C=\overset{+}{S}H$ peak indicates that in this case the exchange of the conjugate acid proton with the solvent proton is slowed down to a large extent even at room temperature.

For N-allylthiourea solutions in HSO_3Cl peaks attributable to the conjugate acid protons ($C=\overset{+}{S}H$) and unaffected NH and NH_2 protons along-with other peaks have been observed. The $C=SH^+$ peak was not quite sharp presumably due to a slow exchange with the solvent proton. The NH_2 peak was a broad triplet (J_{HN}14 = 45 c.p.s.) which may be due to the quadrupole moment of the nitrogen atom.[106] It is, thus apparent that N-allylthiourea undergoes monoprotonation at the sulphur atom of the thioketo groups also consistent with

the conductometric measurements where a γ value of 1.00 has been observed.

The spectrum of N,N'-diisopropylthiourea solution in chlorosulphuric acid shows three peaks at 1.83δ ,3.26δ and 4.08δ with the relative area 11.70:1.00:2.10 respectively assigned to $C-CH_3$, $C=SH^+$ and CH protons respectively. The conjugate acid proton ($C=SH^+$) peak was sharp indicating a very slow exchange with the solvent. The absence of NH proton peak and the broad solvent peak suggests that after the monoprotonation at sulphur atom a partial protonation at nitrogen atom may also be occurring which exchange rapidly with the solvent proton resulting in the broadening of the solvent peak. This observation is consistent with the conductometric results where also a partial diprotonation (γ= 1.16) has been indicated.

For 2,5-dithiobiurea in HSO_3Cl only peaks at 8.50δ and 10.30δ of relative areas 1:2 respectively alongwith a broad solvent peak were observed. Their most reasonable assignment could be to the unaffected NH_2 and NH protons in the molecule. It is therefore, concluded that the diprotonation indicated by the conductivity measurements (γ= 1.90) must be occurring at the two sulphur atoms of the thioketo-groups.

Ultra-Violet Spectroscopic Studies: The two lowest energy transitions for the carbonyl group are a weak $n \rightarrow \pi^*$ transition ($\varepsilon \sim 10^2$) and another relatively strong $\pi \rightarrow \pi^*$ transition ($\varepsilon \sim 10^3$). In molecules having an unperturbed carbonyl group for example in propionaldehyde[107] the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions occur at 270 n.m. and 147 n.m. respectively. In amides the lone pair orbital at nitrogen atom participates in the delocalized π system extending over nitrogen, carbon and oxygen atoms, and perturbs the carbonyl transitions resulting in a large blue shift in the $n \rightarrow \pi^*$ band to 222 n.m and a large red shift in the $\pi \rightarrow \pi^*$ band to about 173 to 200 n.m. It has been shown[39] that if the protonation is occurring at the nitrogen atom then due to the nonavailability of the lone pair orbital of this atom for interaction with the rest of the π system there should be a large red shift in the $n \rightarrow \pi^*$ band and a large blue shift in the $\pi \rightarrow \pi^*$ band. If on the other hand the protonation is occurring at oxygen atom there should be a large red shift in the $\pi \rightarrow \pi^*$ band.

For solutions of urea, thiourea, 1,3-dimethylurea and tetramethylurea in chlorosulphuric acid none of the two bands were observed (Table -19). This is similar to the behaviour of thiourea and S-methylisothiourea in sulphuric acid where also no band was observed.[33] This has been

TABLE - 19

Ultraviolet spectra of the compounds in alcohol and chlorosulphuric acid at 25°C.

Compound	Solvent			
	Alcohol		HSO_3Cl	
	λ (n.m.)	ϵ	λ(n.m.)	ϵ
Urea		No peak	No peak	-
1,3-dimethylurea	"	"	"	"
Tetramethylurea	215	662	No peak	
Cyanoacetylurea	211	347	293	623
1,3-diphenylurea	206	7333	290	1483
	254	17073	-	-
1,3-di-1-naphthylurea	215	9506	298	8556
	305	873	-	-
Thiourea	208	2111	No peak	
	239	3020	-	
1,3-diphenylthiourea	210	17073	-	-
	272	5555	290	6469
N-allylthiourea	209	6332	-	-
	240	4715	290	844
N,N'-diallylthiourea	215	23044	-	-
	240	9410	290	1239
N,N'-diisopropylthiourea	210	9803	-	-
	240	6034	283	1591
2,5-dithiobiurea	265*	2503	292	2016

* band observed in Dimethyl sulphoxide.

interpreted in favour of sulphur protonation. The results of the present studies suggest the formation of a conjugate acid having the proton on the oxygen or sulphur atom.

For cyanoacetyl urea in FSO_3Cl a large red shift in the $\pi \rightarrow \pi^*$ band of the C=O chromophore has been noted strongly suggesting O-protonation. This has also been supported by n.m.r studies.

In the case of 1,3-diphenylurea and 1,3-di-1-naphthylurea two bands, one attributable to the $\pi \rightarrow \pi^*$ of C=O group and the other to the benzenoid absorption[108,109] (at 254 n.m. for benzene and 305 n.m. for naphthalene) were observed in alcoholic solutions. In chlorosulphuric acid however, only one band at around 290 n.m. has been observed for 1,3-diphenylurea and 1,3-di-1-naphthylurea and has been assigned to the $\pi \rightarrow \pi^*$ transition of the C=O group. This band is red shifted by about 85 n.m. from its position in alcohol and is similar to the band observed for cyanoacetylurea in FSO_3Cl suggesting the formation of O-protonated species. The 290 n.m. band could not be the benzenoid band which has most probably disappeared in FSO_3Cl as has also been found in the case of benzamide solution in sulphuric acid[110] of varying strengths where this band either disappeared or was only slightly red shifted ($\sim$ 10 n.m.).

It is apparent from Table -19 that the $\pi \rightarrow \pi^*$ band of the C=S chromophore in N-allylthiourea, N,N'-diallylthiourea, N,N'-diisopropylthiourea and 2,5-dithiobiurea is largely red shifted in HSO_3Cl. For 1,3-diphenylthiourea the band at 272 n.m. observed in its alcoholic solution could be assigned to both the $\pi \rightarrow \pi^*$ of C=S group and to the benzenoid absorption. The $\pi \rightarrow \pi^*$ transition of C=S chromophore being completely masked by benzenoid absorption. However, in the acid solution a band at 290 n.m. attributable to $\pi \rightarrow \pi^*$ of C=S is observed which is largely red shifted from its position in alcoholic solution. The benzenoid band must have disappeared.

The observed red shift in the $\pi \rightarrow \pi^*$ band in the above compounds rules out N-protonation, thus pointing to sulphur protonation.

CHAPTER - IV:

BEHAVIOUR OF CARBAZIDES, CARBAZONES AND THEIR THIO ANALOGUES IN CHLOROSULPHURIC ACID.

INTRODUCTION

The behaviour of carbazides, carbazones and their thio analogues are well known with regard to the formation of their complexes with metal ions. It has been shown that 1,5-diphenylcarbazide, 1,5-diphenylcarbazone and 1,5-diphenylthiocarbazone usually form coloured complexes in solutions[111-113] and it is only due to this behaviour that 1,5-diphenylthiocarbazone has been extensively used as a reagent for the identification of traces of metals colorimetrically.[114] Recently, protonation of 1,5-diphenylthiocarbazone in aqueous sulphuric acid has been reported.[115] However, the behaviour of the rest of the above mentioned compounds have not yet been studied in strong acidic media.

It was considered of interest to study the behaviour of these compounds in HSO_3Cl with a view to determining the site of protonation as well as their basicity. Phenylsemicarbazide, 1,5-diphenylcarbazide, 1,5-diphenylcarbazone, 1,5-diphenylthiocarbazone, 1,4-diphenylsemicarbazide and 1,4-diphenyl-3-thiosemicarbazide were chosen for this study with the help of conductometric, ultra-violet and nuclear magnetic resonance spectroscopic techniques.

PREPARATION AND PURIFICATION OF REAGENTS

Phenylsemicarbazide m.p. 167°C (Rhodia, France), 1,4-diphenylsemicarbazide m.p. 180°C, 1,4-diphenyl-3-thiosemicarbazide m.p. 170°C (Eastman Kodak reagents), 1,5-diphenylcarbazone m.p. 147°C (E.Merck) 1,5-diphenylcarbazide m.p. 170°C and 1,5-diphenylthiocarbazone m.p.113°C with decomposition (B.D.H. England), were used as received.

TABLE - 20

Specific conductance of solutions of phenylsemicarbaside in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 92.5062 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1677
0.1517	0.1997
0.3674	0.2396
0.7273	0.3275
1.0850	0.3835
1.3270	0.4314
1.5820	0.4793
1.7250	0.5164

EXPERIMENT - 2: 80.9850 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1659
0.0554	0.1837
0.2225	0.2077
0.4824	0.2636
0.8860	0.3435
1.1880	0.4166
1.4660	0.4726
1.6620	0.5025
1.8560	0.5353

TABLE - 21

Specific conductance of solutions of 1,4-diphenylsemicarbazide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 101.5016 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1687
0.0513	0.1792
0.1526	0.2018
0.5018	0.2231
0.8762	0.3599
1.2560	0.4363
1.3120	0.4498
1.5630	0.4825
1.6560	0.5165

EXPERIMENT - 2: 59.9806 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1677
0.0927	0.1838
0.2290	0.2167
0.3980	0.2538
0.6629	0.3102
1.1130	0.4097
1.4180	0.4665
1.5290	0.4929
1.7420	0.5334

TABLE - 22

Specific conductance of solutions of 1,4-diphenyl-3-thiosemicarbazide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 66.6160 gm of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1697
0.0550	0.1773
0.2819	0.2342
0.3755	0.2510
0.7502	0.3334
1.0620	0.4998
1.3380	0.4502
1.6250	0.5108

EXPERIMENT - 2: 48.8182 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1697
0.1273	0.1998
0.5612	0.2892
0.8096	0.3336
1.0490	0.3968
1.2720	0.4409
1.5140	0.4926
1.7220	0.5236

TABLE - 23

Specific conductance of solutions of 1,5-diphenylcarbazide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 100.0050 gm of chlorosulphuric acid initially taken as solvent.

W x 10^2	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1697
0.0701	0.1889
0.1835	0.2140
0.3229	0.2433
0.4798	0.2782
0.5848	0.3035
0.8147	0.3549
1.0410	0.4108
1.2210	0.4425

EXPERIMENT - 2: 66.6656 gm of chlorosulphuric acid initially taken as solvent.

W x 10^2	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1697
0.1241	0.2061
0.2413	0.2246
0.4073	0.2623
0.5305	0.2914
0.7177	0.3375
0.9800	0.4014
1.1180	0.4204
1.4050	0.4825
1.5520	0.5234

TABLE - 24

Specific conductance of solutions of 1,5-diphenylcarbazone in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 95.5106 gm of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1677
0.0880	0.1885
0.2339	0.2237
0.4720	0.2716
0.6678	0.3195
0.8536	0.3675
1.0860	0.4165
1.2150	0.4515

EXPERIMENT - 2: 80.0010 gm of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1677
0.0210	0.1757
0.1437	0.1997
0.3333	0.2396
0.5870	0.3036
0.7299	0.3355
0.9274	0.3835
1.3050	0.4624
1.4160	0.4856
1.5090	0.5031

TABLE - 25

Specific conductance of solutions of 1,5-diphenylthiocarbazone in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 97.5012 gm of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1667
0.0764	0.1901
0.2403	0.2317
0.4827	0.2876
0.7562	0.3627
1.0080	0.4154
1.2530	0.4792
1.4510	0.5268

EXPERIMENT - 2: 50.5118 gm of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1667
0.0184	0.1773
0.1503	0.2077
0.3162	0.2476
0.6877	0.3355
0.8818	0.3835
1.1650	0.4634
1.3440	0.5033
1.5560	0.5495

DISCUSSION

Conductometric Studies: All the solutes have been found to give coloured and highly conducting solutions in chlorosulphuric acid. The colour and conductance of solutions stayed constant for about two days suggesting the formation of stable species in solution.

From Figure-8 it is evident that the specific conductance of phenylsemicarbazide falls on the specific conductance curve of potassium chloride suggesting monoprotonation (γ = 1.00) of this compound. Recently from these laboratories results of spectrophotometric studies on Sn(IV) and Ge(IV) chloride complexes of 1,5-diphenylcarbazide, 1,5-diphenylcarbazone and 1,5-diphenylthiocarbazone have been reported where it has been suggested that coordination to the tin and germanium atoms occurs through the oxygen atom or sulphur atom of the carbonyl or thiocarbonyl group.[111,112] It, therefore, appeared more likely that protonation in these compounds might occur at the oxygen or sulphur atom rather than on the nitrogen atom. For phenylsemicarbazide where monoprotonation is indicated (γ = 1.00) the reaction seems to be as follows:

$$C_6H_5\text{-}NH\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH_2 + HSO_3Cl \rightleftharpoons C_6H_5\text{-}NH\text{-}NH\text{-}\underset{\underset{OH^+}{\|}}{C}\text{-}NH_2 + SO_3Cl^- \quad (34)$$

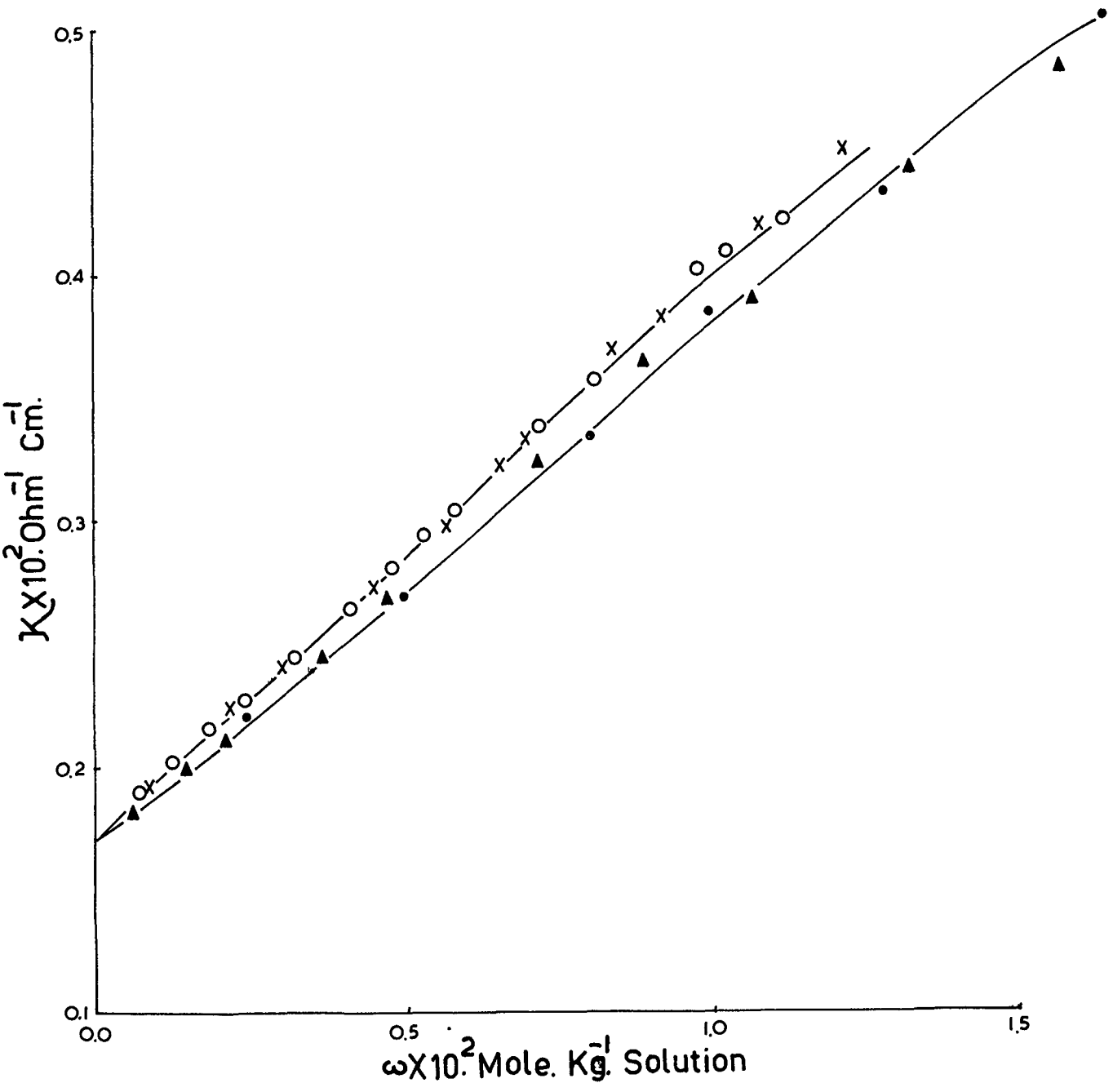
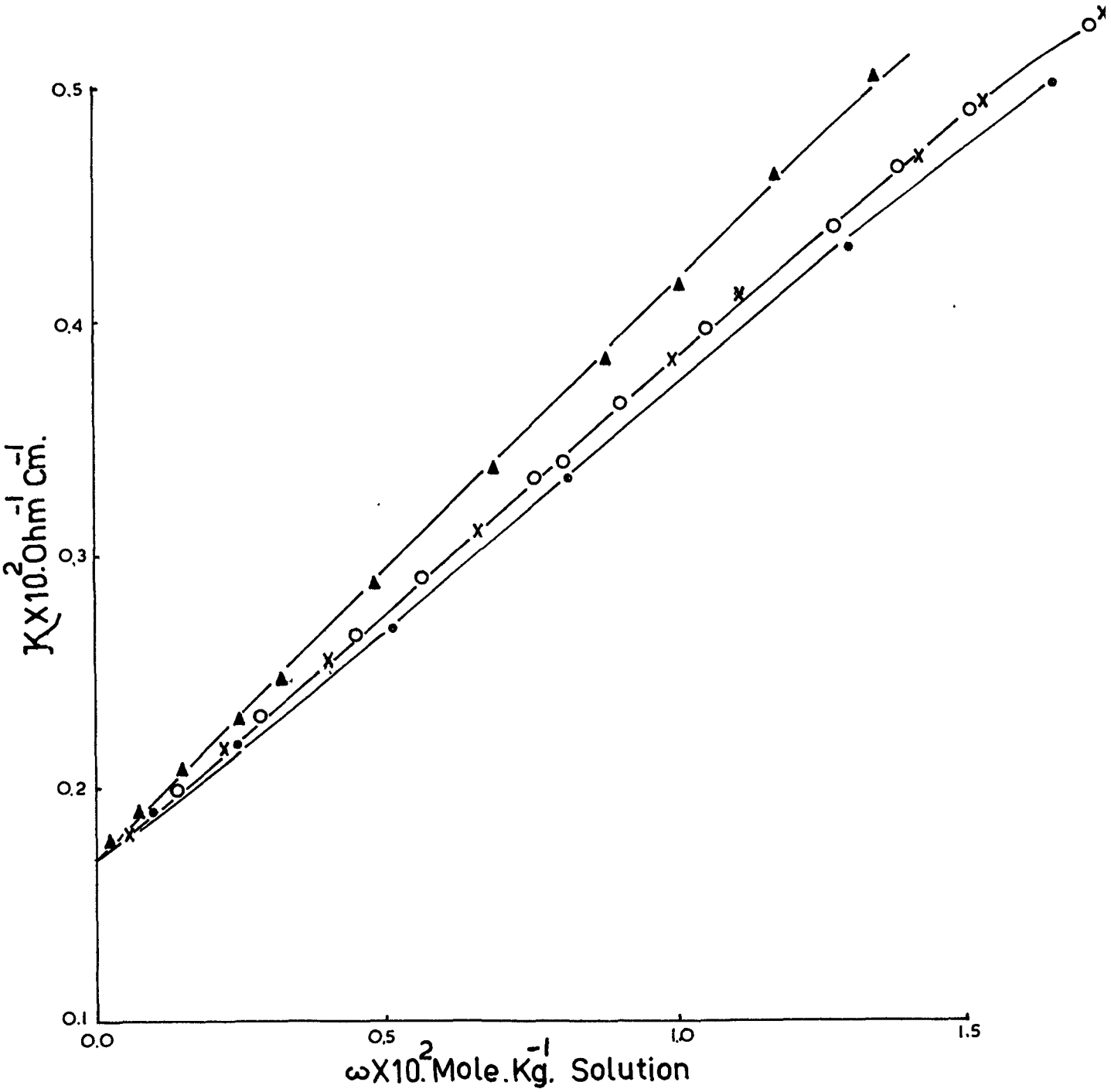

0.5
0.4
0.3
0.2
0.1
0.0
0.5
1.0
1.5
κX10².Ohm⁻¹ Cm⁻¹
ωX10².Mole. Kg⁻¹ Solution
• POTASSIUM CHLORIDE
O 1,5-DIPHENYLCABAZIDE
X 1,5-DIPHENYLCABAZONE
▲ PHENYLSEMICARBAZIDE

Fig.8



- ● POTASSIUM CHLORIDE
- ▲ 1,5-DIPHENYLTHIOCARBAZONE
- X 1,4-DIPHENYLSEMICARBAZIDE
- O 1,4-DIPHENYL-3-THIOSEMICARBAZIDE

Fig.9

From Table -26 it is also evident that 1,5-diphenylcarbazide, 1,5-diphenylcarbazone, 1,5-diphenylthiocarbazone, 1,4-diphenylsemicarbazide and 1,4-diphenyl-3-thiosemicarbazide undergo incomplete diprotonation in FSO_3Cl. The second protonation which is only partial must be occurring at the nitrogen atom. The conductometric data thus suggest that alongwith the oxygen or sulphur atom of carbonyl or thiocarbonyl group the nitrogen atoms attached to these groups are also sufficiently basic to be at least partially protonated.

A relative order of the basicity of these compounds on the basis of the present studies can be written as below:

1,5-diphenylthiocarbazone $>$ 1,5-diphenylcarbazone $\backsim$
1,5-diphenylcarbazide $>$ 1,4-diphenylsemicarbazide $\backsim$
1,4-diphenyl-3-thiosemicarbazide $>$ phenylsemicarbazide.

NMR Spectroscopic Studies: The peaks observed in the n.m.r spectra of compounds in chlorosulphuric acid and $CDCl_3$ have been shown in Table-27. The appearance of a broad solvent peak in the n.m.r. spectra of the compounds in FSO_3Cl has been attributed to a rapid exchange of the proton on the conjugate acid thus formed with that of the solvent proton and also accounts for the absence of the peak attributable to the conjugate acid.

TABLE - 26

Average value of γ calculated from the specific conductances of the compounds in chlorosulphuric acid at 35°C.

Compound	γ
Phenylsemicarbazide	1.00
1,4-diphenylsemicarbazide	1.05
1,4-diphenyl-3-thiosemicarbazide	1.05
1,5-diphenylcarbazide	1.16
1,5-diphenylcarbazone	1.16
1,5-diphenylthiocarbazone	1.25

TABLE - 27

Chemical shifts in p.p.m. for compounds in $CDCl_3$ and HSO_3Cl at 25°C using T.M.S. as external reference.

Compound	Solvent peak	Ph	C=XH⁺	Ph-NH-N-	-N-NH-C(=X)-	Ph-$\overset{+}{N}H_2$-N-	-C(=X)-$\overset{+}{N}H_2$— Ph
Phenylsemicarbazide Ph-NH-NH-C(=O)-NH_2	b	8.58 (7.33)	-	7.63	7.80	-	-
1,4-diphenylsemicarbazide 1 2 3 4 Ph-NH-NH-C(=O)-NH-Ph	b	8.66 (7.33)	-	-	8.00	9.16	-
1,4-diphenyl-3-thiosemicarbazide 1 2 3 4 Ph-NH-NH-C(=S)-NH-Ph	b	8.66 (7.33)	5.33 b	-	8.00	9.16	10.00
1,5-diphenylcarbazide 1 2 3 4 5 Ph-NH-NH-C(=O)-NH-NH-Ph	b	8.66 (7.33)	-	-	7.83	9.46	-
1,5-diphenylcarbazone 1 2 3 4 5 Ph-N=N-C(=O)-NH-NH-Ph	b	8.71 (7.33)	-	-	7.85	9.45	-
1,5-diphenylthiocarbazone 1 2 3 4 5 Ph-N=N-C(=S)-NH-NH-Ph	b	- (7.33)	3.20 S	-	-	-	-

( ) position of the peak in $CDCl_3$

X = O or S, b = broad, S = Sharp.

In the n.m.r. spectra of solutions of phenylsemicarbazide, 1,4-diphenylsemicarbazide, 1,4-diphenyl-3-thiosemicarbazide, 1,5-diphenylcarbazide, 1,5-phenylcarbazone and 1,5-diphenylthiocarbazone in $CDCl_3$ excepting for only one multiplet due to the benzene ring protons no other peak was observed.

The n.m.r. spectra of solutions of 1,5-diphenylcarbazide and 1,5-diphenylcarbazone in chlorosulphuric acid are similar and consist of peaks attributable to C_6H_5, $C_6H_5-\overset{+}{N}H_2-N$, and $N-NH-\underset{O}{C}$ protons alongwith a broad solvent peak. The $N-NH-\underset{O}{C}$ peak is a sharp triplet ($J_{NH,\overset{+}{N}H_2}$ = 9.5 c.p.s) which can not be due to the quadrupole moment of the nitrogen atom[95] since it would have required a J value of ~ 50 c.p.s. and may therefore be due to the spin-spin coupling of the $N-NH-\underset{O}{C}$ proton with the $C_6H_5-\overset{+}{N}H_2-N$ protons. The above described $C_6H_5-\overset{+}{N}H_2-N$ peak is similar to the one observed in the case of N-methylthiourea solution in SbF_5-FSO_3F at -67°C at 8.19δ attributed to the $CH_3-\overset{+}{N}H_2$ protons?[95] The broad solvent peak observed in both the cases viz., 1,5-diphenylcarbazide and 1,5-diphenylcarbazone suggests that there is protonation at carbonyl oxygen atom also. The $C=O\overset{+}{H}$ peak could not be observed due to exchange with the solvent proton. Thus in conclusion there is partial

protonation at nitrogen atom 5 in 1,5-diphenylcarbazone and at both the nitrogen atoms 1 and 5 in 1,5-diphenylcarbazide alongwith complete monoprotonation at the carbonyl oxygen atom. This observation is consistent with the conductometric results where a γ value of 1.16 for both the solutes has been observed.

Solution of 1,5-diphenylthiocarbazone in chlorosulphuric acid gave a sharp $C=\overset{+}{S}H$ peak and a broad peak spanning from 7.66δ to 8.83δ. It was difficult to assign this broad peak. However, the sharp $C=\overset{+}{S}H$ proton peak (not exchanging with the solvent in the present case) and the broad solvent peak suggest some protonation on nitrogen atom also. It is thus clear that in 1,5-phenylthiocarbazone there is protonation at the sulphur atom alongwith partial protonation at the nitrogen atom consistent with the conductometric results (γ = 1.25).

In the chlorosulphuric acid solution of phenylsemicarbazide three peaks of relative area 5.0:1.0:0.9 have been observed and are attributed to the phenyl ring protons, and the protons on the unaffected nitrogen atoms 1 and 2 respectively. No peak attributable to the conjugate acid proton could be observed in this case.

The solution of 1,4-diphenylsemicarbazide in chlorosulphuric acid gave three peaks at 8.00δ, 8.66δ and 9.16δ attributable to N-NH-C(=O), C_6H_5 and C_6H_5-$\overset{+}{N}H_2$-N protons respectively. The protonation at nitrogen atom 1 i.e. the presence of C_6H_5-$\overset{+}{N}H_2$-N peak is further confirmed by the splitting of the unaffected N-NH-C(=O) proton peak into a triplet ($J_{NH,\overset{+}{N}H_2}$ = 9.5 c.p.s). A broad solvent peak suggests further protonation but its site could not be fixed which could be either the carbonyl oxygen or the nitrogen atom 4 or both.

For 1,4-diphenyl-3-thiosemicarbazide in HSO_3Cl, peaks attributable to C=$\overset{+}{S}$H, N-NH-C(=S), C_6H_5, C_6H_5-$\overset{+}{N}H_2$-N and C(=$\overset{+}{N}H_2$)-C_6H_5 have been observed. The C=SH^+ peak was not quite sharp presumably due to a slow proton exchange with the solvent as indicated by the broadening of the solvent peak. Protonation at nitrogen atom 1 is confirmed by the splitting of unaffected N-NH-C(=S) proton peak into a sextet. This may presumably be due to its splitting first by C_6H_5-$\overset{+}{N}H_2$-N protons into a triplet ($J_{NH,\overset{+}{N}H_2}$ = 9.5 c.p.s) and then by C=$\overset{+}{S}$H proton into a sextet (J_{NH,SH^+} = 7.5 c.p.s).

Ultra-Violet Spectroscopic Studies: The results of the ultraviolet spectroscopic studies of the carbazides and carbazones have been shown in Table-28.

TABLE - 28

Ultraviolet spectra of the compounds in alcohol and chlorosulphuric acid at 25°C.

Compound	Solvent			
	Alcohol		HSO_3Cl	
	λ(n.m.)	ϵ	λ(n.m.)	ϵ
Phenylsemicarbazide	232	4456	280	3210
	279	329	290	787
1,5-diphenylcarbazide	233	3798	280	6876
	280	623	291	1249
1,4-diphenylsemicarbazide	236	32200	280	3665
	274	203	289	656
1,4-diphenyl-3-thiosemicarbazide	235	8273	282	7986
1,5-diphenylcarbazone	229	11182	283	4922
	285	1625	295	2052
1,5-diphenylthiocarbazone	245	5288	285	6528

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Since all these compounds have the carbonyl or the thiocarbonyl functions as in urea, the two lowest energy transitions in these compounds too would be the $\pi \rightarrow \pi^*$ ($\epsilon \sim 10^3$) and $n \rightarrow \pi^*$ ($\epsilon \sim 10^2$). Oxygen or sulphur protonation in these compounds would result in a large red shift in the $\pi \rightarrow \pi^*$ band.[39]

For semicarbazones and thiosemicarbazones in inert solvent the band observed at about 225 to 230 n.m. has been attributed to the $\pi \rightarrow \pi^*$ transition of the C=O or C=S chromophore.[116,117] For 1,5-diphenylcarbazone, and 1,5-diphenylthiocarbazone the band at 229 n.m. and 245 n.m. respectively in the alcoholic solutions of these compounds may therefore be attributed to the $\pi \rightarrow \pi^*$ transition. The band observed at around 230 n.m. for alcoholic solutions of 1,5-diphenylcarbazide, 1,4-diphenylsemicarbazide, 1,4-diphenyl-3-thiosemicarbazide, and phenylsemicarbazide is assigned to the $\pi \rightarrow \pi^*$ transition. In chlorosulphuric acid solution of these compounds this band is largely red shifted to about 280 n.m. ($\epsilon \sim 10^3$) which suggests oxygen or sulphur protonation. The secondary or benzenoid absorption occurring at about 280 n.m. ($\epsilon \sim 10^2$) in the alcoholic solutions of 1,5-diphenylcarbazide, phenylsemicarbazide, 1,5-diphenylcarbazone and 1,4-diphenylsemicarbazide is slightly red

shifted (∽ 10 n.m.) in the acid. A red shift in the benzenoid absorption of about the same magnitude has also been reported in the case of benzamide solution in concentrated H_2SO_4[110].

CHAPTER - V:

BEHAVIOUR OF HYDRAZINES IN CHLOROSULPHURIC ACID

INTRODUCTION

It is well-known that in aqueous solution only hydrazonium ion (NH_2-NH_3^+) exists as a stable species and the diprotonated species NH_3^+-NH_3^+ has not been found to be stable in aqueous solution.[118] Recently, from conductometric studies on solutions of hydrazine dihydrochloride in chlorosulphuric acid Robinson and Ciruna[23] have shown that this compound behaves as a strong base and forms a stable diprotonated species. Phenylhydrazine which is also expected to behave as a strong base in strong acidic media has however, been shown to yield an incompletely monoprotonated conjugate acid in fluorosulphuric acid.[26] It, therefore, prompted the author to study the behaviour of hydrazine sulphate, phenylhydrazine, and a few substituted phenylhydrazines viz., 2-nitrophenylhydrazine, 4- nitrophenylhydrazine, 2,4-dinitrophenylhydrazine and 2,5-dichlorophenylhydrazine in chlorosulphuric acid with a view to determining their basicity with regard to the formation of dipositive species and examining the effect of substitution on the basicity of various hydrazines.

PREPARATION AND PURIFICATION OF REAGENTS

Purification of reagents:

Phenylhydrazine (Riedel) was redistilled and the fraction distilling at 243°C was collected.

4-Nitrophenylhydrazine m.p.158°C with decomposition (E.Merck), 2-nitrophenylhydrazine m.p.90°C (Fluka, A.G), 2,4-dinitrophenylhydrazine m.p. 195°C (B.D.H., England), 2,5-dichlorophenylhydrazine m.p. 105°C (Koch-Light) and hydrazine sulphate m.p. 254°C (B.D.H., England) were used as received.

TABLE - 29

pecific conductance of solutions of phenylhydrazine in hlorosulphuric acid at 35°C.

XPERIMENT - 1: 70.5252 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$\chi \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1707
0.056	0.1814
0.662	0.3850
1.106	0.5825
1.713	0.8121
2.347	1.0640
3.116	1.3020
3.896	1.5470
4.509	1.7110

XPERIMENT - 2: 61.5168 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$\chi \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1707
0.251	0.2348
0.967	0.5530
1.308	0.6649
2.058	0.9395
2.753	1.1950
3.505	1.4380
4.252	1.6530
4.995	1.8320

TABLE - 30

Specific conductance of solutions of 4-nitrophenylhydrazine in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 55.5860 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1714
0.096	0.1995
0.815	0.4690
1.469	0.7349
1.762	0.8400
2.109	0.9589
2.948	1.2600
3.699	1.4920
4.451	1.7060

EXPERIMENT - 2: 73.3126 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1707
0.348	0.2940
1.176	0.6090
1.553	0.7705
1.952	0.9099
2.589	1.1260
3.412	1.4060
4.108	1.6130
4.858	1.7950

TABLE - 31

Specific conductance of solutions of 2-nitrophenylhydrazine in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 73.3250 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1697
0.269	0.2258
0.734	0.3287
1.208	0.4336
1.777	0.5597
2.416	0.7031
3.375	0.9027
4.411	1.1150
6.275	1.4720

EXPERIMENT - 2: 49.9856 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1702
0.531	0.2845
0.917	0.3707
1.444	0.4918
2.099	0.6366
2.920	0.7872
3.788	0.9832
5.252	1.2590
6.758	1.5530

TABLE - 32

Specific conductance of solutions of 2,4-dinitrophenyl-hydrazine in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 51.2124 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.000	0.1707
0.187	0.1988
0.569	0.2758
0.994	0.3437
1.795	0.5033
2.518	0.6362
3.163	0.7903
3.987	0.9301
5.254	1.1890

EXPERIMENT - 2: 82.3620 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.000	0.1707
0.072	0.1777
0.375	0.2338
0.781	0.3073
1.258	0.3962
2.048	0.5488
2.841	0.6958
3.509	0.8323
4.663	1.0620
5.962	1.3210

TABLE - 33

Specific conductance of solutions of 2,5-dichlorophenylhydrazine in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 81.8124 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.000	0.1707
0.187	0.1930
0.564	0.2594
1.045	0.3505
2.068	0.5486
3.394	0.7980
4.620	1.0260
5.952	1.2940
6.416	1.4020

EXPERIMENT - 2: 61.6008 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1} cm^{-1}$
0.000	0.1707
0.307	0.2140
0.843	0.3050
1.414	0.4184
1.752	0.4782
2.536	0.6410
3.995	0.9209
5.253	1.1400
6.844	1.4750

TABLE - 34

Specific conductance of solutions of hydrazine sulphate in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 55.6432 gm. of chlorosulphuric acid initially taken as solvent.

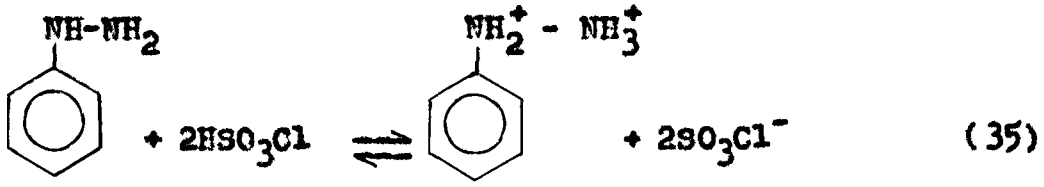
W x 10^2	K x 10^2 ohm^{-1}cm^{-1}
0.000	0.1684
0.844	0.3930
1.541	0.5913
2.302	0.8080
2.954	0.9905
3.498	1.1520
4.516	1.3720
5.471	1.6060
6.674	1.8570

EXPERIMENT - 2: 49.8968 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	K x 10^2 ohm^{-1}cm^{-1}
0.000	0.1684
0.558	0.3012
1.256	0.5086
1.807	0.7103
2.619	0.8962
3.174	1.0360
3.952	1.2350
5.026	1.4980
6.171	1.7480
7.058	1.9470

DISCUSSION

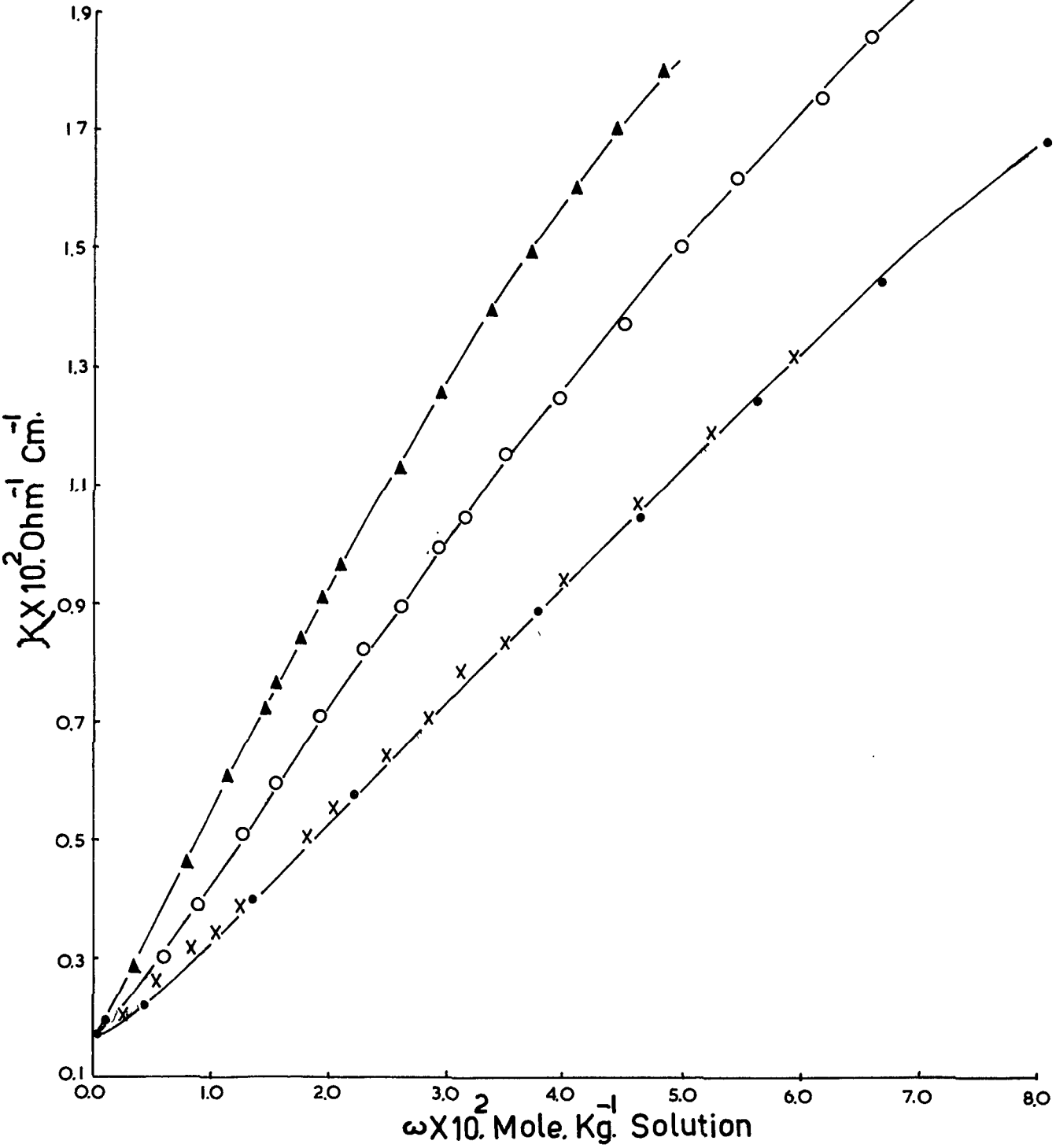
All the hydrazines have been found to behave as simple strong bases in chlorosulphuric acid. They produced conducting solutions (Figures 10 and 11) which stayed stable for a long period (about 3-4 days). It is evident from Table -35 that phenylhydrazine undergoes complete diprotonation ($\gamma = 2.00$) according to the following mode of ionization;



(35)

Even in sulphuric acid[119] which is weaker than chlorosulphuric acid a complete diprotonation of phenylhydrazine has been indicated. It is rather surprising that in fluorosulphuric acid Paul and coworkers[26] have observed an incomplete monoprotonation of this compound. The basicities of the other substituted phenylhydrazines have been compared with that of phenylhydrazine and have been summarized in Table-35.

In the case of 4-nitrophenylhydrazine a complete diprotonation ($\gamma = 2.00$) has been observed. It is reasonable



- POTASSIUM CHLORIDE
- 4-NITROPHENYLHYDRAZINE
- HYDRAZINE SULPHATE
- X 2,4-DINITROPHENYLHYDRAZINE

Fig.10

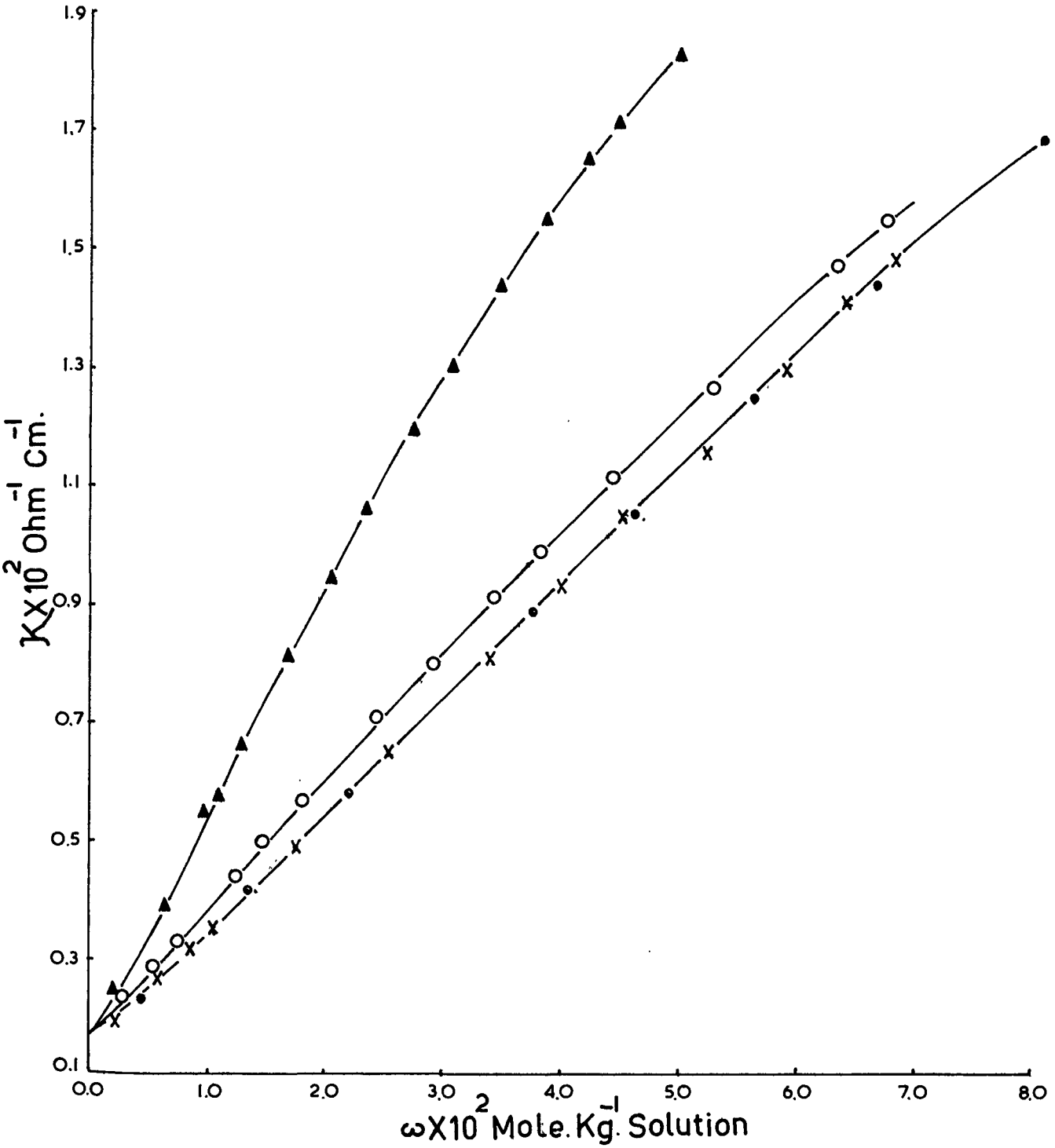

1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
κX10² Ohm⁻¹ Cm⁻¹
ωX10² Mole.Kg⁻¹ Solution
• POTASSIUM CHLORIDE
▲ PHENYLHYDRAZINE
O 2-NITROPHENYLHYDRAZINE
X 2,5-DICHLOROPHENYLHYDRAZINE

Fig.11

TABLE - 35

Average value of γ calculated from the specific conductances of the compounds in chlorosulphuric acid at 35°C.

Compound	γ
Phenylhydrazine	2.00
4-nitrophenylhydrazine	2.00
2-nitrophenylhydrazine	1.15
2,4-dinitrophenylhydrazine	1.00
2,5-dichlorophenylhydrazine	1.00
Hydrazine sulphate	1.50

to suggest that after protonation at hydrazine nitrogen atoms further protonation at nitro group becomes improbable due to -I affect of the $-NH_2^+$ $-NH_3^+$ group. A similar observation has also been found in the case of ortho and para nitroanilines in sulphuric acid[120] where it has been shown that protonation occurs at NH_2 group only. In 2-nitrophenylhydrazine the extent of protonation is very low (γ = 1.15) as compared to that observed for phenylhydrazine and 4-nitrophenylhydrazine. This decrease in the basicity of the former compound can be explained by considering the following factors.

(i) The -I effect of nitro group which is more effective at the ortho position may decrease appreciably the basicity of hydrazine nitrogen atoms.

(ii) There may be the formation of ion-pairs after protonation at hydrazine nitrogen atoms. This would reduce the concentration of free SO_3Cl^- ions in the solution and would thus cause an appreciable decrease in the conductivity of the solution. Ion-pairs formation in chlorosulphuric acid may be favoured due to its low dielectric constant (ϵ = 60) and it has been shown that it accounts the appreciable decrease in the ionization of alkali metal halides and chlorosulphates in this solvent.[23]

With the introduction of one more nitro group a further decrease in the basicity of hydrazine nitrogen atoms has been observed such as, for example, in 2,4-dinitrophenylhydrazine where only monoprotonation (γ = 1.00) has been indicated. In 2,5-dichlorophenylhydrazine also monoprotonation (γ = 1.00) is observed. This may be assigned to the decrease in the basicity due to inductive (-I) effect of the chlorine atoms as well as to the formation of ion-pairs.

In the case of hydrazine sulphate a γ value of 1.50 has been observed. It is reasonable to suggest that this compound ionizes in chlorosulphuric acid in two steps. In the first step there is formation of a monoprotonated species $NH_2-NH_3^+$ according to the following reaction:

$$NH_2-NH_2\cdot H_2SO_4 + HSO_3Cl \rightleftharpoons NH_2-NH_3^+ + SO_3Cl^- + H_2SO_4 \quad (36)$$

In the second step, protonation of $NH_2-NH_3^+$ occurs resulting in the formation of a diprotonated hydrazine as given by the following reaction:

$$NH_2-NH_3^+ + HSO_3Cl \rightleftharpoons NH_3^+ - NH_3^+ + 2SO_3Cl^- \quad (37)$$

It has been indicated that this diprotonated species does not exist as a stable entity in aqueous medium but is

converted into the monoprotonated form. As the conductance of the solutions does not change with passage of time it therefore, suggests that in chlorosulphuric acid NH_3^+-NH_3^+ remains stable and does not dissociate to any other form. When equations (36) and (37) are taken together a γ value of 2.00 is required for this reaction as given by equation (38).

$$NH_2\text{-}NH_2\cdot H_2SO_4 + H_2SO_4 \rightleftharpoons NH_3^+ - NH_3^+ + 2SO_3Cl^- + H_2SO_4 \quad (38)$$

However, the observed lower value of γ from that predicted by equation (38) may presumably be due to the formation of ion-pairs.

A relative order of the basicity of the compounds on the basis of present studies can be written as-

Phenylhydrazine $\backsim$ 4-nitrophenylhydrazine $\rangle$ hydrazine sulphate $\rangle$ 2-nitrophenylhydrazine $\rangle$ 2,4-dinitrophenylhydrazine $\backsim$ 2,5-dichlorophenylhydrazine.

CHAPTER - VI:

BEHAVIOUR OF INORGANIC ACID ANHYDRIDES AND ACID HALIDES IN CHLOROSULPHURIC ACID

INTRODUCTION

Solutions of nitric acid, dinitrogen pentoxide and metallic nitrates have since long been known to be efficient reagents in aromatic nitration.[121] The species responsible for nitration was considered to be the nitronium ion. However, the existence of this cationic species as a stable entity was first indicated by Gillespie and coworkers.[43] Evidences for the existence of the oxycations NO^+ and NO_2^+ as a stable species in solutions started accumulating with conductometric, cryoscopic, i.r. and Raman studies on the solutions of nitric acid, dinitrogen pentoxide and metal nitrates in concentrated sulphuric acid.[44,45,122]

Very recently, formation of the oxycations NO^+ and NO_2^+ from the ionization of the anhydrides of the oxyacids of nitrogen N_2O_3 and N_2O_5 respectively in strong acidic media[46,123] $H_2S_2O_7$ and HSO_3F has been indicated. Similar attempts to prepare in strong acidic media the oxycations of other elements of group V i.e. P, As, Sb, Bi and V and of group VI i.e. Se and Te have been successful only in the case of arsenic trioxide in sulphuric acid.[47]

Although chlorosulphuric acid is a stronger acid than sulphuric acid no such study has so far been reported in this solvent. It was, therefore, considered worthwhile to study the behaviour of the oxides of As, Sb, Bi, P, V, Se and Te in chlorosulphuric acid with a view to exploring the possibility of the formation and stabilization of the oxycations of these elements.

It has been found that the oxycations NO^+ and NO_2^+ could also be obtained by the ionization of the oxyhalides NOCl, NOF and NO_2Cl in disulphuric acid.[124] Another possible route to the formation of such oxycations thus appeared to be the direct ionization of the oxyhalides and therefore the behaviour of the oxyhalides of Sb, Bi, P and V in chlorosulphuric acid has also been examined.

PREPARATION AND PURIFICATION OF REAGENTS

Purification of reagents:

Phosphoryl chloride (Riedel) was redistilled and the fraction distilling at 108°C was collected.

Arsenic trioxide, vanadium pentoxide (E.Merck), antimony trioxide pure (Reachim,U.S.S.R.), bismuth trioxide pure (Chemapol, Czechoslovakia), selenium dioxide (Johnson Matthey, England), phosphorus pentoxide(Riedel), antimony oxychloride, arsenic pentoxide and niobium pentoxide (B.D.H., England) were used after drying in vacuum at 100°C.

Preparation of reagents:-

Antimony pentoxide[125] was prepared by adding 5 gm. of antimony pentachloride (Riedel) in 100 ml. of cold distilled water. The white precipitate thus obtained was washed with water and filtered. It was then dried at 275°C to a constant weight to give a fine yellow powder of Sb_2O_5.

Bismuth oxychloride[126] A solution of 3 gm. of bismuth trioxide in 300 ml. of hydrochloric acid (density 1.08) was heated to boiling. It was then poured into 2.5 litre of boiling water and the boiling was continued until the

initial precipitate redissolved in the solution. It was then allowed to cool. A colourless crystalline mass was obtained after filtration which was dried in vacuum at 100°C.

Bismuth oxybromide[127]: A solution of 3 gm. of bismuth trioxide in 50 ml. of hydrobromic acid (density 1.38) was heated to boiling. It was then diluted with 1.5 litre of boiling distilled water and boiling was continued until the initial precipitate redissolved. Colourless crystalline powder of BiOBr was crystallized out on cooling in ice. It was washed with HBr and then with cold water and dried in vacuum at 100°C.

Bismuth oxyiodide[127]: A solution of 0.50 gm. of bismuth trioxide in 40 ml. of hydroiodic acid (density 1.2) was diluted with 6 litre of water. The whole solution was heated on a water bath. Brick-red coloured crystalline powder of BiOI immediately precipitated. It was filtered and dried in vacuum at 100°C.

Vanadyl chloride[128]: It was prepared by refluxing vanadium pentoxide (E.Merck) with thionyl chloride(Riedel) according to the following reaction:

$$V_2O_5 + 3SOCl_2 \longrightarrow 2VOCl_3 + 3SO_2 \qquad (39)$$

20 gm. of vanadium pentoxide and 24 ml. of thionyl chloride were taken in a flask connected with a reflux condenser. It was heated for 6 to 8 hours on a water bath under anhydrous condition. The product was distilled and the material boiling at 127°C was collected.

Tellurium dioxide[129] It was prepared by the action of nitric acid with tellurium powder (B.D.H., England) according to the reaction:

$$2Te + 9HNO_3 \longrightarrow Te_2O_3(OH)NO_3 + 8NO_2 + 4H_2O$$

$$Te_2O_3(OH)NO_3 \xrightarrow[400^oC]{\Delta} 2TeO_2 + HNO_3 \qquad (40)$$

In a beaker containing a suspension of 5 gm. of tellurium powder in 200 ml. of distilled water, 95 ml. of concentrated HNO_3 (density 1.42) was slowly added. It was then allowed to stand for 30 minutes with occasional shaking. To remove insoluble impurities it was suction filtered and the filtrate was again mixed with 65 ml. of concentrated HNO_3 (density 1.42). The solution was boiled until all oxides of nitrogen were removed and the solution was concentrated to 100 ml. on a water bath. At this stage the

crystals of $Te_2O_3(OH)NO_3$ separated which were filtered, washed with water and dried in air. It was, then further heated for about two hours at 430°C on a hot plate to obtain white crystals of TeO_2.

TABLE - 36

Specific conductance of solutions of potassium chloride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 60.6100 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1399
0.791	0.2835
1.306	0.3990
2.190	0.5881
2.795	0.7499
3.759	0.9466
5.617	1.2600
7.394	1.5760

EXPERIMENT - 2: 55.1240 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1404
0.931	0.3156
1.679	0.4759
2.581	0.6791
3.262	0.8215
4.872	1.1340
6.382	1.3950
8.068	1.6520

TABLE-37

Specific conductance of solutions of arsenic trioxide in chlorosulphuric acid at 35°C

EXPERIMENT - 1: 55.5106 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1544
1.280	0.1553
3.351	0.1644
4.827	0.1679
6.156	0.1750
7.350	0.1819
8.198	0.1829
9.434	0.1882

EXPERIMENT - 2: 40.0080 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1544
2.194	0.1609
2.556	0.1618
4.258	0.1649
5.501	0.1705
7.012	0.1803
8.556	0.1910
10.840	0.1952

TABLE - 38

Specific conductance of solutions of antimonytrioxide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 47.7612 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1605
1.138	0.1925
1.869	0.2274
2.701	0.2660
4.055	0.3359
5.186	0.3920
7.066	0.4830
8.270	0.5249

EXPERIMENT - 2: 55.5102 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1644
0.562	0.1714
1.552	0.2102
2.314	0.2498
3.383	0.3010
4.592	0.3605
6.215	0.4405
7.515	0.5040
9.292	0.5650

TABLE - 39

Calculations for the determination of the dissociation constant (K_b) of $SbO.SO_3Cl$ formed in solutions of antimonytrioxide in chlorosulphuric acid at 35°C.

w	C_s	γ	$K_b \times 10^3$ Moles. Kg^{-1}
0.0113	0.0030	0.263	0.41
0.0186	0.0050	0.267	0.56
0.0270	0.0070	0.259	1.04
0.0338	0.0085	0.251	1.12
0.0405	0.0105	0.258	1.46
0.0459	0.0127	0.245	1.57
0.0518	0.0130	0.250	1.71
0.0621	0.0150	0.241	2.05
0.0706	0.0165	0.233	2.17
0.0751	0.0175	0.232	2.29
0.0827	0.0185	0.223	2.28
0.9290	0.0210	0.226	2.06

Average value of $K_b = 1.56 \times 10^{-3}$ Moles.Kg^{-1}

TABLE - 40

Specific conductance of solutions of bismuth trioxide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 66.6610 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1409
0.0325	0.1494
0.4143	0.2404
0.9656	0.3663
1.7050	0.5049
2.4150	0.6301
3.7190	0.7599
5.0750	0.8440

EXPERIMENT - 2: 71.1112 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2 ohm^{-1} cm^{-1}$
0.0000	0.1409
0.1481	0.1760
0.6629	0.3019
1.3910	0.4524
1.9090	0.5470
2.9170	0.6790
4.3780	0.7949
5.5140	0.8506

TABLE - 41

Calculations for the determination of the dissociation constant (K_b) of $BiO.SO_3Cl$ formed in solutions of bismuth trioxide in chlorosulphuric acid at 35°C.

W	C_s	γ	$K_b \times 10^3$ Moles.$Kg.^{-1}$
0.0139	0.0152	1.092	18.28
0.0171	0.0175	1.027	18.49
0.0191	0.0200	1.047	21.97
0.0241	0.0230	0.952	22.26
0.0292	0.0260	0.891	20.88
0.0372	0.0300	0.806	19.38
0.0438	0.0315	0.719	17.24
0.0508	0.0340	0.669	17.08

Average value of $K_b = 19.43 \times 10^{-3}$ Moles.$Kg.^{-1}$

TABLE - 42

Specific conductance of solutions of antimony oxychloride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 60.1200 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1}cm^{-1}$
0.000	0.1704
0.892	0.1806
1.470	0.1889
3.425	0.2324
4.281	0.2590
6.532	0.3150
7.927	0.3569
9.838	0.4095

EXPERIMENT - 2: 50.0026 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2 ohm^{-1}cm^{-1}$
0.0000	0.1714
0.3274	0.1750
0.9516	0.1808
1.5580	0.2016
2.3110	0.2098
5.3890	0.2869
5.9060	0.3011
6.8520	0.3226
8.0590	0.3606

TABLE - 43

Calculations for the determination of the dissociation constant (K_b) of $SbO.SO_3Cl$ formed in solutions of antimony oxychloride in chlorosulphuric acid at 35°C.

w	C_s	γ	$K_b \times 10^3$ Moles.$Kg.^{-1}$
0.0089	0.0025	0.280	0.97
0.0147	0.0035	0.217	0.97
0.0343	0.0040	0.216	1.10
0.0428	0.0065	0.151	1.15
0.0539	0.0080	0.148	1.39
0.0653	0.0095	0.145	1.61
0.0793	0.0112	0.141	1.83
0.0984	0.0135	0.137	2.14

Average value of $K_b = 1.40 \times 10^{-3}$ Moles.$Kg.^{-1}$

TABLE - 44

Specific conductance of solutions of bismuth oxychloride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 80.8212 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1470
0.2676	0.1819
0.6313	0.2345
1.0330	0.2869
1.6050	0.3502
3.5100	0.5389
4.9670	0.6579
6.4090	0.7849
8.1710	0.9325

EXPERIMENT - 2: 71.0188 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1470
0.5013	0.2117
0.8512	0.2660
1.3510	0.3096
2.9460	0.4865
4.4150	0.6195
5.8150	0.7279
7.0410	0.8420

TABLE - 45

Calculations for the determination of the dissociation constant (K_b) of $BiO.SO_3Cl$ formed in solutions of bismuth oxychloride in chlorosulphuric acid at 35°C.

w	C_s	γ	$K_b \times 10^3$ Moles.Kg^{-1}
0.0063	0.0047	0.752	14.36
0.0085	0.0065	0.763	20.92
0.0103	0.0077	0.750	23.25
0.0160	0.0105	0.656	20.02
0.0295	0.0170	0.577	23.18
0.0351	0.0195	0.555	24.32
0.0442	0.0235	0.532	26.71
0.0497	0.0253	0.508	24.03
0.0582	0.0285	0.490	27.38
0.0641	0.0310	0.483	24.30

Average value of $K_b = 22.84 \times 10^{-3}$ Moles.Kg^{-1}

TABLE - 46

Specific conductance of solutions of bismuth oxybromide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 42.4420 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1470
0.542	0.2170
1.308	0.3006
2.018	0.3858
2.612	0.4557
3.551	0.5396
3.863	0.5670
5.058	0.6682
7.091	0.8303

EXPERIMENT - 2: 60.0052 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1465
0.051	0.1707
1.084	0.2835
1.628	0.3464
2.346	0.4263
2.918	0.4759
4.690	0.6439
6.185	0.7599
8.063	0.8991

TABLE - 47

Calculations for the determination of the dissociation constant (K_b) of $BiO.SO_3Cl$ formed in solutions of bismuth oxybromide in chlorosulphuric acid at 35°C.

ω	C_s	γ	$K_b \times 10^3$ Moles.Kg^{-1}
0.0054	0.0040	0.739	11.32
0.0108	0.0073	0.659	14.01
0.0163	0.0105	0.644	18.99
0.0235	0.0145	0.618	23.45
0.0292	0.0165	0.565	21.43
0.0386	0.0210	0.546	25.25
0.0469	0.0245	0.522	26.75
0.0619	0.0300	0.485	28.25
0.0709	0.0330	0.465	28.67
0.0806	0.0365	0.452	30.10

Average value of $K_b = 22.82 \times 10^{-3}$ Moles.Kg^{-1}

TABLE - 48

Specific conductance of solutions of bismuth oxyiodide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 86.8500 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1509
0.378	0.2015
1.164	0.2980
2.164	0.4085
3.058	0.4953
4.213	0.6129
5.582	0.7284
6.761	0.8124

EXPERIMENT - 2: 63.3982 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1509
0.198	0.1775
0.636	0.2335
1.605	0.3469
2.674	0.4590
3.859	0.5781
4.837	0.6584
6.066	0.7705
7.419	0.8685

TABLE - 49

Calculations for the determination of the dissociation constant (K_b) of $BiO.SO_3Cl$ formed in solutions of bismuth oxyiodide in chlorosulphuric acid at 35°C.

w	C_s	γ	$K_b \times 10^{-3}$ Moles.Kg^{-1}
0.0038	0.0028	0.727	7.32
0.0064	0.0045	0.707	10.85
0.0116	0.0080	0.687	17.52
0.0161	0.0108	0.669	21.72
0.0216	0.0130	0.660	19.50
0.0267	0.0155	0.579	21.30
0.0306	0.0173	0.564	22.30
0.0386	0.0215	0.557	27.20
0.0421	0.0225	0.534	25.70
0.0484	0.0250	0.516	26.60
0.0558	0.0285	0.510	29.60
0.0607	0.0300	0.494	29.40
0.0676	0.0320	0.473	28.70
0.0742	0.0350	0.471	31.10

Average value of $K_b = 22.77 \times 10^{-3}$ Moles.Kg^{-1}

TABLE - 50

Specific conductance of solutions of phosphorous pentoxide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 100.9810 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1467
0.5564	0.3198
0.9586	0.4958
1.7520	0.8014
2.2750	1.0130
3.4180	1.3250
4.5520	1.6320
5.5060	1.8490

EXPERIMENT - 2: 98.8600 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1487
0.264	0.2340
0.700	0.4075
1.245	0.6279
1.763	0.8850
3.024	1.2240
3.875	1.4860
5.220	1.7450
6.358	2.0050

TABLE - 51

Specific conductance of solutions of phosphoryl chloride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 100.0060 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1644
0.949	0.1784
2.465	0.2106
3.707	0.2305
4.756	0.2505
6.018	0.2818
7.409	0.2975
8.483	0.3114
10.487	0.3407

EXPERIMENT - 2: 69.9816 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1644
1.860	0.1960
3.057	0.2240
4.180	0.2450
5.390	0.2624
6.505	0.2835
8.051	0.3007
9.795	0.3324
11.306	0.3569

TABLE - 52

Calculations for the determination of the dissociation constant (K_{BH^+}) of the conjugate acid formed in solutions of phosphoryl chloride in chlorosulphuric acid at 35°C.

C_w	C_s	α	$K_{BH^+} \times 10^4$ Moles.Kg.$^{-1}$
0.0095	0.0020	0.210	5.31
0.0186	0.0030	0.164	5.88
0.0306	0.0040	0.138	6.40
0.0418	0.0055	0.131	8.29
0.0539	0.0065	0.120	8.86
0.0651	0.0075	0.115	9.74
0.0741	0.0080	0.108	9.68
0.0848	0.0090	0.106	10.66

Average value of K_{BH^+} = 8.10×10^{-4} Moles.Kg.$^{-1}$

TABLE - 53

Specific conductance of solutions of seleniumdioxide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 88.8062 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1575
0.108	0.1889
0.647	0.2869
1.276	0.4060
1.793	0.5080
2.287	0.6160
2.796	0.7069
4.426	1.0500
7.072	1.5240

EXPERIMENT - 2: 95.0682 gm. of chlorosulphuric acid initially taken as solvent.

$W \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1575
0.359	0.2415
1.112	0.3765
1.271	0.4025
2.024	0.5670
2.792	0.7139
3.559	0.8780
5.801	1.2600
8.251	1.6990

TABLE - 54

Specific conductance of solutions of telluriumdioxide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 70.0712 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1468
0.2804	0.1995
0.8514	0.3227
1.5710	0.5040
2.4650	0.7139
3.1100	0.8762
4.1560	1.0820
5.0520	1.2520

EXPERIMENT - 2: 49.9850 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1470
0.0391	0.1540
0.4963	0.2485
1.0370	0.3814
2.3330	0.6790
2.6840	0.7949
3.7700	1.0090
4.4140	1.1440
5.4940	1.3440

TABLE - 55

Specific conductance of solutions of vanadium pentoxide in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 120.2028 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1312
0.1088	0.1387
0.2654	0.1397
0.3113	0.1397
0.4715	0.1425
0.9749	0.1567
1.2050	0.1602
2.6680	0.1639

EXPERIMENT - 2: 100.8604 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1399
0.0740	0.1399
0.1942	0.1399
0.5305	0.1470
0.8743	0.1505
1.7360	0.1550
2.4010	0.1580
3.0950	0.1645

TABLE - 56

Specific conductance of solutions of potassium chloride in chlorosulphuric acid containing 0.01 molar of vanadium pentoxide at 35°C.

100.2686 gm. of chlorosulphuric acid containing 0.01 molar of vanadium pentoxide was initially taken.

$\omega \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1767
0.2261	0.2080
0.9839	0.3068
2.7130	0.6045
4.3490	0.8644
5.6010	1.1050
7.2390	1.3640
8.7130	1.6180
10.2700	1.8460

TABLE - 57

Specific conductance of solutions of vanadyl chloride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 100.6864 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1609
2.056	0.1625
3.422	0.1644
5.026	0.1644
5.846	0.1666
6.008	0.1702
7.358	0.1756

EXPERIMENT - 2: 110.1028 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1702
2.348	0.1731
5.659	0.1746
7.898	0.1754
17.682	0.1852

TABLE - 58

Specific conductance of solutions of potassium chloride in chlorosulphuric acid containing 0.17 molon of vanadyl chloride at 35°C.

60.2436 gm. of chlorosulphuric acid containing 0.17 molon of vanadylchloride was initially taken.

$W \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1852
0.508	0.2268
1.088	0.3022
2.917	0.5362
4.520	0.7670
5.756	0.9485
6.717	1.0790
7.652	1.1420
8.692	1.3640

TABLE - 59

Average value of dissociation constant (K_b) of oxychlorosulphates calculated from specific conductances of the compounds in chlorosulphuric acid at 35°C.

Compound	$K_b \times 10^3$ Moles.Kg^{-1}
Antimony trioxide	1.56
Antimony oxychloride	1.40
Bismuth trioxide	19.43
Bismuth oxychloride	22.84
Bimuth oxybromide	22.82
Bismuth oxyiodide	22.77

DISCUSSION

Arsenic trioxide dissolved extensively in chlorosulphuric acid with the evolution of hydrogen chloride gas yielding a very low conducting solution (γ = 0.05) Table-60. The evolution of hydrogen chloride rules out the possibility of the formation of conjugate acid BH^+ (i.e. protonation of As_2O_3) in which case no HCl should be formed as shown by the following equation:

$$As_2O_3 + HSO_3Cl \rightleftharpoons [As_2O_3H]^+ + SO_3Cl^- \qquad (41)$$

The low conductivity of the solution indicates a very small concentration of free SO_3Cl^- which is suggested to be present either as a solvolysed species $As(SO_3Cl)_3$ or as $ASO{\cdot}SO_3Cl$ after the following mode of ionization:

$$As_2O_3 + 9HSO_3Cl \rightleftharpoons 2As(SO_3Cl)_3 + 3H_2SO_4 + 3HCl\uparrow \qquad (42)$$

$$As_2O_3 + 3HSO_3Cl \rightleftharpoons 2ASO{\cdot}SO_3Cl + H_2SO_4 + HCl\uparrow \qquad (43)$$

One would have expected the formation of $As(SO_3Cl)_3$ on the analogy of the formation of $As(SO_3F)_3$ in FSO_3F[123] The species $As(SO_3Cl)_3$ if being formed should have behaved as a weak acid in chlorosulphuric acid solvent by consuming one chlorosulphate ion according to the following equation:

$$As(SO_3Cl)_3 + SO_3Cl^- \rightleftharpoons As(SO_3Cl)_4^- \qquad (44)$$

TABLE - 60

Average value of γ calculated from specific conductances of the compounds in chlorosulphuric acid at 35°C.

Compound	γ
arsenic trioxide	0.05
Antimony trioxide	0.25
Bismuth trioxide	0.90
Phosphorous pentoxide	2.00
Selenium dioxide	1.00
Tellurium dioxide	1.10
Antimony oxychloride	0.18
Bismuth oxychloride	0.61
Bismuth oxybromide	0.57
Bismuth oxyiodide	0.58
Phosphoryl chloride	0.14

and causing a decrease in the conductance of the solution with the passage of time. As there is no such decrease in the conductance of the solution, ionization represented by equation (42) must be ruled out. The low conductance of the solution (Figure-12) should therefore, be due to the formation of the very weak bases H_2SO_4[130] and HCl[23] of chlorosulphuric acid solvent system. The low conductance further suggests that $ASO.SO_3Cl$ formed does not ionise appreciably to produce the cation ASO^+.

Apparently there is some evidence for the formation of the hithertofore elusive oxycations of Sb and Bi viz. SbO^+ and BiO^+ on dissolving antimony trioxide and bismuth trioxide respectively in chlorosulphuric acid. Antimony trioxide was fairly soluble in chlorosulphuric acid with the evolution of hydrogen chloride gas and gave solutions having stable conductivities for about 24 hours. The following mode of ionisation is suggested for its reaction:

$$Sb_2O_3 + 3HSO_3Cl \rightleftharpoons 2(SbO.SO_3Cl) + H_2SO_4 + HCl\uparrow$$

$$2(SbO.SO_3Cl) \rightleftharpoons 2SbO^+ + 2SO_3Cl^- \qquad (45)$$

For the ionisation given by equation(45) a γ value of about 2.00 is required whereas the observed value is only 0.25. This suggests that the oxychlorosulphate

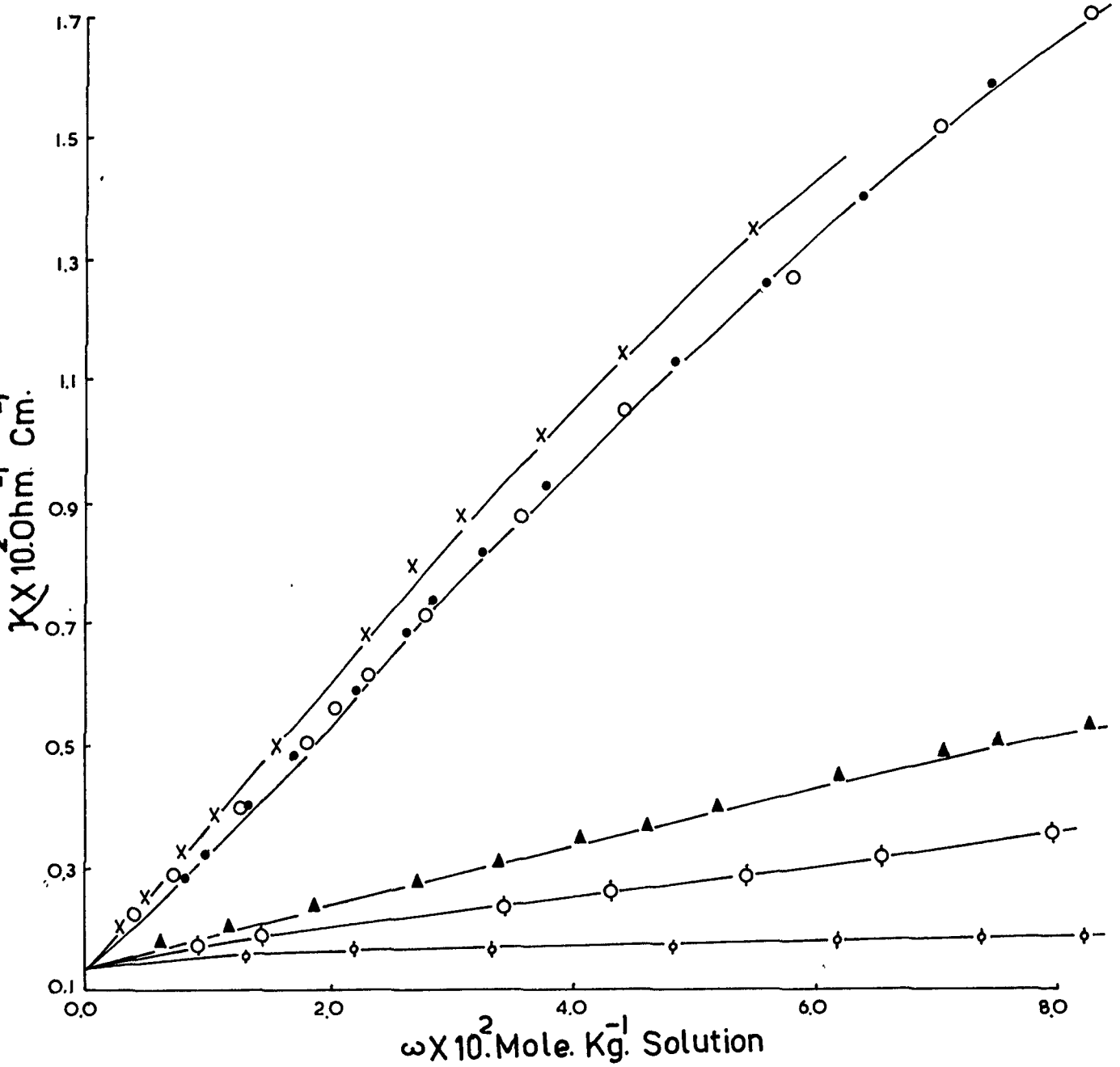

1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
0.0
2.0
4.0
6.0
8.0
κX 10² Ohm⁻¹ Cm⁻¹
ωX 10² Mole. Kg⁻¹ Solution
• POTASSIUM CHLORIDE
O SELENIUM DIOXIDE
X TELLURIUM DIOXIDE
▲ ANTIMONY TRIOXIDE
ϕ ANTIMONY OXYCHLORIDE
ϕ ARSENIC TRIOXIDE

Fig.12

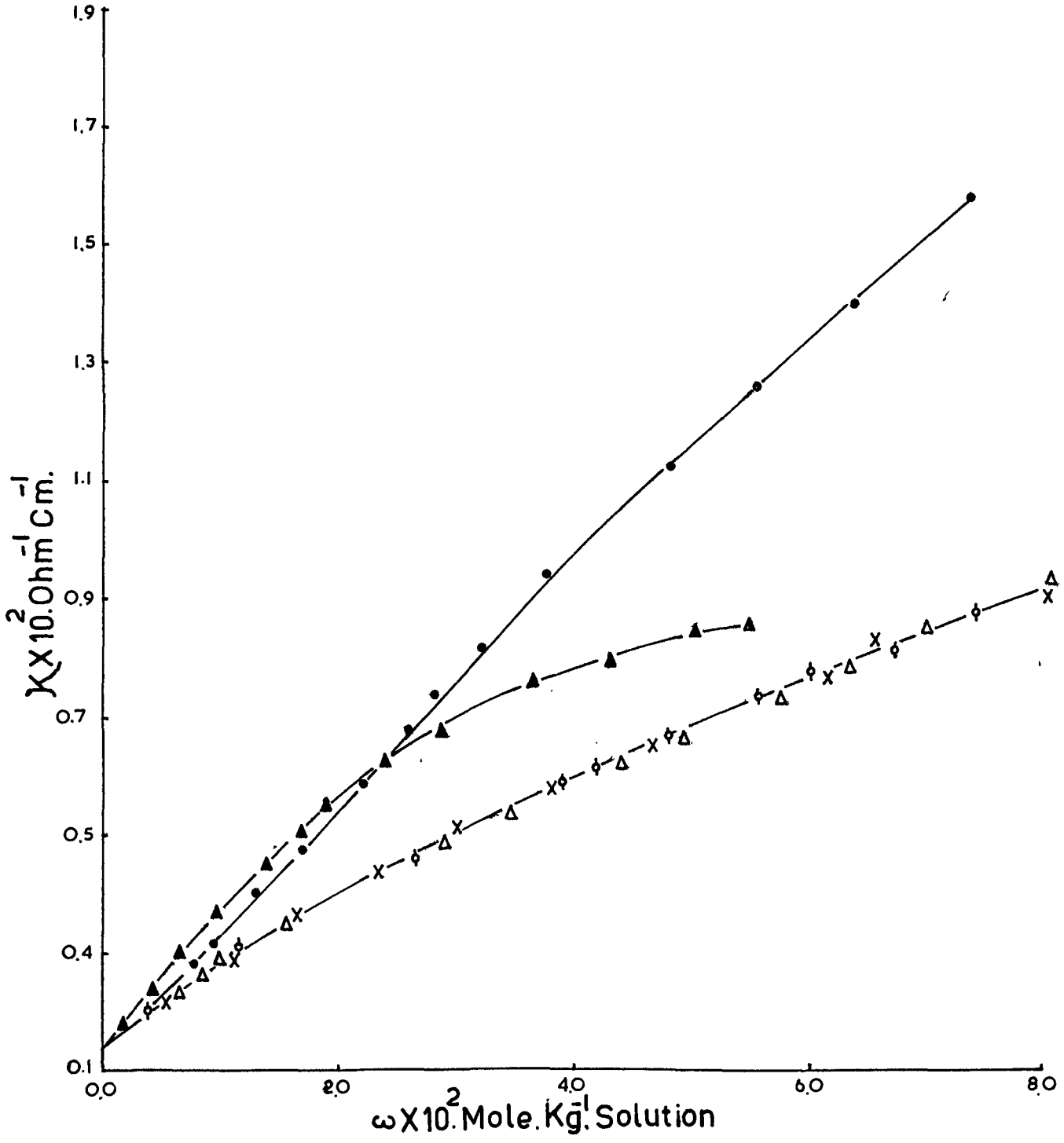

1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.4
0.1
0.0
2.0
4.0
6.0
8.0
κX10².Ohm⁻¹Cm.⁻¹
ωX10².Mole.Kg⁻¹.Solution
POTASSIUM CHLORIDE
BISMUTH TRIOXIDE
BISMUTH OXYCHLORIDE
BISMUTH OXYBROMIDE
BISMUTH OXYIODIDE

Fig.13

formed in the first step of equation(45) is weakly ionized to produce the SbO^+ cation. A decrease in γ value with increasing concentrations of the antimony trioxide was observed (Table-39) which may presumably be due to the polymerization of the unionized oxychlorosulphates into $[SbO.SO_3Cl]_2$ analogous to the formation of $[AsO.SO_4H]_2$ in sulphuric acid.[47] The dissociation constant of the oxychlorosulphate ($SbO.SO_3Cl$) has been calculated from the observed γ values by the use of the relationship given below:

$$K_b = \frac{[SbO^+][SO_3Cl^-]}{[SbO.SO_3Cl]}$$

$$\text{or} = \frac{\gamma[SO_3Cl^-]}{(2-\gamma)} \qquad (46)$$

$$\text{since } [SO_3Cl^-] = \frac{C_s}{2} + \sqrt{(\frac{C_s}{2})^2 + K_{ap}}$$

Where C_s is the concentration of a strong electrolyte (e.g. KCl) at the same specific conductance of the solute having concentration $\underline{a}$ and K_{ap} is the autoprotolysis constant of the chlorosulphuric acid. Since the acid has a very low conductance contribution from the K_{ap} would be

small and may be neglected[23]. Equation(46) may, therefore, be written as follows:

$$K_b = \frac{\gamma C_s}{(2 - \gamma)} \qquad (47)$$

The average value of K_b obtained for $SbO.SO_3Cl$ has been shown in Table-59.

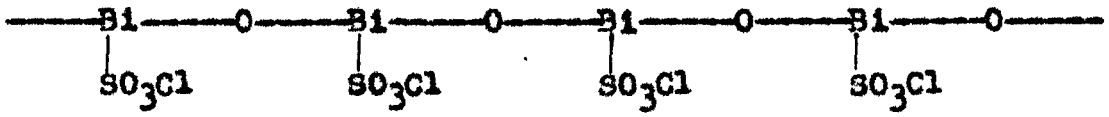
Bismuth trioxide also gave stable and highly conducting solution (γ = 0.90) in chlorosulphuric acid. Its ionization is analogous to that of Sb_2O_3 (equation 45) and may be represented as follows:

$$Bi_2O_3 + 3HSO_3Cl \rightleftharpoons 2BiO.SO_3Cl + H_2SO_4 + HCl\uparrow$$

$$2BiO.SO_3Cl \rightleftharpoons 2BiO^+ + 2SO_3Cl^- \qquad (48)$$

A decrease in the γ value from 1.10 to 0.67 with increasing concentrations of the solute has been observed upto 0.05 molons. At concentrations above 0.02 molons there appeared a solid which was separated but could not be characterized as it could not be isolated free from the acid. These observations suggest that at low concentration (below 0.02 molons) there is ionization of $BiO.SO_3Cl$ to give the cationic species BiO^+. The average

value of the dissociation constant of $BiO.SO_3Cl$ has been evaluated using equation (47). However, the formation of a precipitate even in quite dilute solution (0.02 molons) of bismuth trioxide is consistent with the formation presumably of a long chain polymer $(BiO.SO_3Cl)_n$ which may be represented as below:



The oxyhalides of antimony and bismuth were soluble and gave solutions having stable conductances ($\gamma \simeq 0.2$ and 0.6 for SbOCl and BiOX respectively, X is Cl, Br, and I). At higher concentrations a solid was obtained from the solutions of antimony oxychloride and bismuth oxyhalides which could not be characterized in either case. In these solutions also a decrease in the γ value with increasing concentrations of the solutes has been noted. These observations are consistent with the following mode of ionization;

$$SbOCl + HSO_3Cl \rightleftharpoons SbO.SO_3Cl + HCl\uparrow$$
$$SbO.SO_3Cl \rightleftharpoons SbO^+ + SO_3Cl^- \qquad (49)$$

$$BiOX + HSO_3Cl \rightleftharpoons BiO.SO_3Cl + HX\uparrow$$
$$BiO.SO_3Cl \rightleftharpoons BiO^+ + SO_3Cl^- \qquad (50)$$

where in the first step low ionizing oxychlorosulphates are formed which then partly ionize to give the oxycations similar to those observed for their trioxides. The decrease in the γ value with increasing concentrations of the solutes in these cases too is attributable to the polymerization of the unionized oxychlorosulphates. The dissociation constants of the oxychlorosulphates of antimony and bismuth produced according to equation (49) and (50) respectively, have been calculated from the relation:

$$K_b = \frac{\gamma [SO_3Cl^-]}{(1-\gamma)} \qquad (51)$$

since $[SO_3Cl^-] = \frac{C_s}{2} + \sqrt{(\frac{C_s}{2})^2 + K_{sp}}$

or $\simeq C_s$

Hence $K_b = \frac{\gamma C_s}{(1-\gamma)}$ (52)

It is apparent from Table-59 that the average K_b values of oxychlorosulphates obtained from both, the ionization of oxyhalides and the corresponding trioxides are quite comparable. This supports the representation of the mode of ionization of the oxides by equation(45) and (48) and those of the oxyhalides by equation (49) and (50).

Attempt to obtain further evidence for the existence of SbO^+ and BiO^+ species from i.r. studies did not prove to be of much help as no band was observed in the spectrum of the solutions of Sb_2O_3, Bi_2O_3, SbOCl, BiOCl, BiOBr and BiOI in HSO_3Cl. This may be due to the masking of these bands by the strong background absorption of the solvent and polyethylene in 1500-1000 cm^{-1} region, where one might expect these bands.

Arsenic pentoxide and antimony pentoxide which were also considered to produce AsO_2^+ and SbO_2^+ cations respectively on dissolving in chlorosulphuric acid however, remained insoluble indicating no interaction with the acid.

It has been shown that phosphorus pentoxide dehydrates strong acidic solvents like disulphuric acid[46] and fluorosulphuric acid[123] producing very low conducting solutions. However, in chlorosulphuric acid quite a different behaviour of phosphorus pentoxide has been observed. It dissolved yielding stable and highly conducting solutions (γ = 2.00) with the evolution of hydrogen chloride gas. Its ionization in chlorosulphuric acid is, thus represented by equation(53) as given below:

$$P_2O_5 + 11HSO_3Cl \rightleftharpoons 2H_4PO_4^+ + 4S_2O_5Cl_2 + 2SO_3Cl^- + H_2SO_4 + HCl\uparrow \qquad (53)$$

Recently, from ^{31}P n.m.r. spectroscopic studies on solutions of phosphorus pentoxide in strong acidic media[131], it has been revealed that concentrated solutions of phosphorus pentoxide in chlorosulphuric acid contain protonated phosphoric acid, trimetaphosphoric acid and a few higher phosphoric acids. It is reasonable to suggest that at higher concentrations of phosphorus pentoxide the protonated phosphoric acid formed (equation 53) is condensed to give higher acids.

Phosphoryl chloride has been studied in strong acids viz. sulphuric[132] and fluorosulphuric[26] acids and has been found to be a non-electrolyte in H_2SO_4 and a weak electrolyte in HSO_3F. In chlorosulphuric acid however, it produces a stable low conducting solution (Figure-14). As there is no evolution of hydrogen chloride gas any ionization scheme involving formation of HCl is ruled out. It is reasonable to suggest that in this case protonation occurs at the oxygen atom to give the conjugate acid $^{+}HO{=}PCl_3$ after the following mode of ionization:

$$POCl_3 + HSO_3Cl \rightleftharpoons {}^{+}HO = PCl_3 + SO_3Cl^{-} \qquad (54)$$

The extent of protonation ($\gamma = 0.14$) suggests it to be a weak base. The basic dissociation constant (K_{BH^+}) of the conjugate acid $^{+}HOPCl_3$ has been calculated by using the

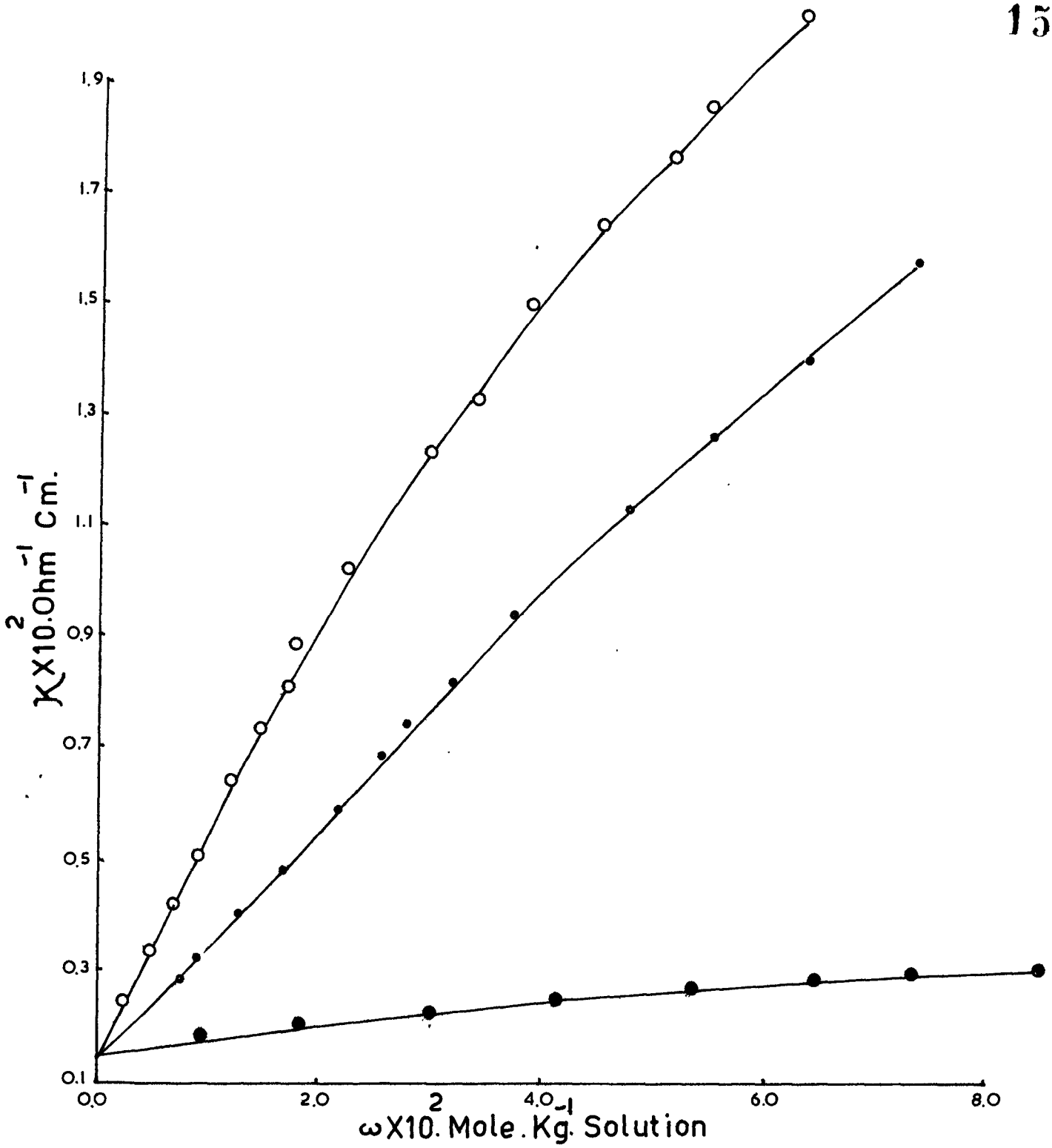

1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
$\kappa_2 X10.Ohm^{-1} cm.^{-1}$
0.0
2.0
4.0
6.0
8.0
$\omega X10^2. Mole.Kg.^{-1} Solution$
• POTASSIUM CHLORIDE
○ PHOSPHORUS PENTOXIDE
● PHOSPHORYL CHLORIDE

Fig.14

the following expression which is analogous to that used by Gillespie and coworkers[56] for weak bases in fluorosulphuric acid.

$$K_{BH^+} = \frac{[BH^+][SO_3Cl^-]}{[B]} \qquad (55)$$

If α is the extent of ionization of base B in the acid to give the conjugate acid BH^+ then

$$[B] = (1 - \alpha)$$

and $$[BH^+] = \alpha$$

If C_s is the concentration of a strong electrolyte (e.g. KCl) in HSO_3Cl at the same specific conductance of the weak base having concentration C_w

$$\text{then} \quad \alpha = \frac{C_s}{C_w}$$

$$\text{and} \quad [SO_3Cl^-] = \frac{C_s}{2} + \sqrt{\left(\frac{C_s}{2}\right)^2 + K_{ap}}$$

where K_{ap} is the autoprotolysis constant of chlorosulphuric acid and as mentioned earlier may be neglected.

thus

$$[SO_3Cl^-] = C_s$$

substituting the concentrations of BH^+, B and SO_3Cl^- in equation (55) we have

$$K_{BH^+} = \frac{\alpha . C_s}{(1-\alpha)}$$

or

$$= \frac{\alpha^2 . C_w}{(1-\alpha)} \qquad (56)$$

The average value of K_{BH^+} obtained by using equation(56) is 8.10×10^{-4} Moles.$Kg.^{-1}$

Vanadium pentoxide was found to have a limited solubility in chlorosulphuric acid and a solution of upto 0.03 molon concentration only could be obtained. It gave a brown-red coloured solution with evolution of hydrogen chloride gas and produced a very small change in the conductance of the solvent unlike its behaviour in sulphuric acid[132,133] where it gave highly conducting solutions. Since vanadium is known to form compounds of the type VOX_3, it seems reasonable to postulate the following reaction of V_2O_5:

$$V_2O_5 + 9HSO_3Cl \rightleftharpoons 2\,[VO(SO_3Cl)_3] + 3H_2SO_4 + 3HCl\uparrow \qquad (57)$$

Vanadyl chloride also gave brown-red coloured solutions in HSO_3Cl with no appreciable change in the conductance of the

solvent. The following solvolytic reaction similar to equation (57) is suggested for vanadyl chloride:

$$VOCl_3 + 3HSO_3Cl \rightleftharpoons VO(SO_3Cl)_3 + 3HCl\uparrow \qquad (58)$$

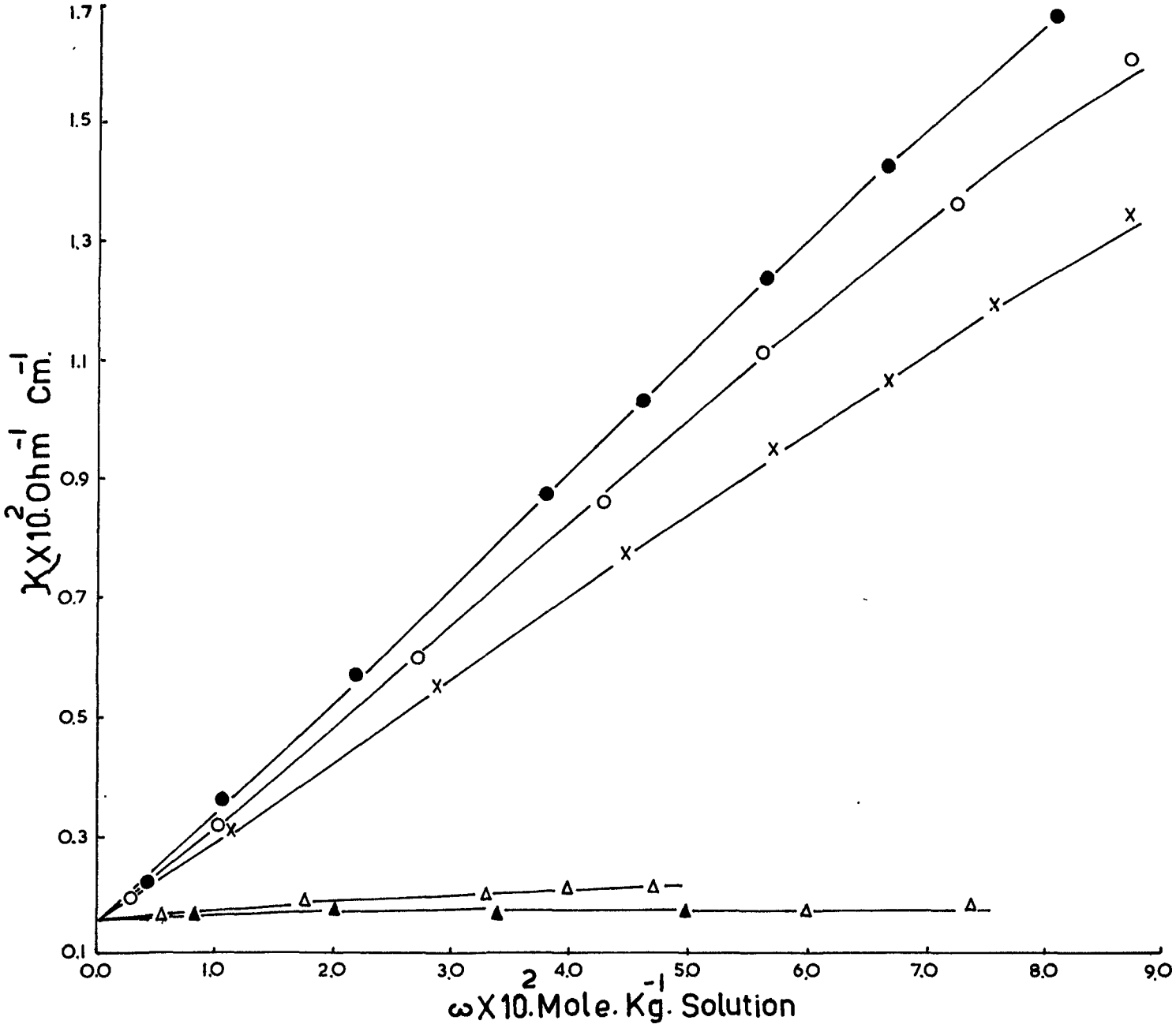
When a strong electrolyte viz. potassium chloride was added to the solutions of vanadium pentoxide and vanadyl chloride in chlorosulphuric acid, the slope of the specific conductance-concentration curve (Figure-15) of potassium chloride was observed to be lowered from its value observed in neat chlorosulphuric acid. This decrease is attributable to the mopping up of the chlorosulphate ions, produced in the solutions by the species $VO(SO_3Cl)_3$ according to the following reaction:-

$$VO(SO_3Cl)_3 + SO_3Cl^- \rightleftharpoons VO(SO_3Cl)_4^- \qquad (59)$$

This observation provides support to the suggested modes of ionization of vanadium pentoxide and vanadyl chloride according to equation (57) and (58) respectively.

Niobium pentoxide remained insoluble in chlorosulphuric acid without producing any change in the conductance of the solvent suggesting no interaction whatsoever.

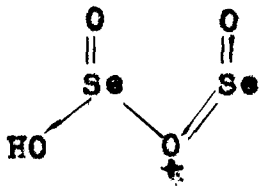
It has been known for many years that selenium dioxide dissolves in sulphuric acid[134] to give a bright yellow



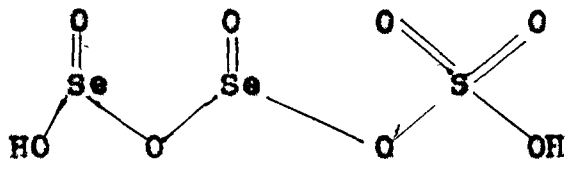
● POTASSIUM CHLORIDE
Δ VANADIUM PENTOXIDE
▲ VANADYL CHLORIDE
O POTASSIUM CHLORIDE IN 0.01ω V_2O_5
X POTASSIUM CHLORIDE IN 0.17ω $VOCl_3$

Fig.15

coloured solution. Its behaviour in sulphuric acid as a weak base was first indicated by Flowers and coworkers[135] They further suggested that in dilute solution of selenium dioxide in sulphuric acid the ion $HSe_2O_4^+$ (I) is also present together with unionized diselenioushydrogensulphate, $Se_2O_3(OH)(HSO_4)$ (II).



I



II

In chlorosulphuric acid selenium dioxide was extensively soluble resulting in the formation of bright yellow coloured solution which was stable and highly conducting (γ = 1.00). There was no evolution of hydrogen chloride gas. The ionization of selenium dioxide in chlorosulphuric acid may therefore, be represented as:

$$O = Se = O + HSO_3Cl \rightleftharpoons O = Se = OH^+ + SO_3Cl^- \quad (60)$$

The observed γ value of 1.00 suggests a complete monoprotonation of selenium dioxide in chlorosulphuric acid.

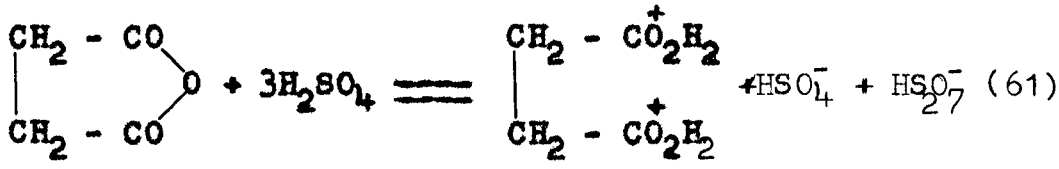
Tellurium dioxide has been found to be insoluble in sulphuric acid.[1] However, in chlorosulphuric acid it was fairly soluble and gave stable and highly conducting solutions (γ = 1.10). The observed γ value suggests that there is a partial diprotonation in tellurium dioxide. Its ionization is essentially similar to that of selenium dioxide (equation 60) where one of the oxygen atom is completely protonated. The next diprotonation in TeO_2 which is incomplete might however, be occurring at the second oxygen atom.

CHAPTER - VII:

BEHAVIOUR OF ORGANIC ACID ANHYDRIDES IN CHLOROSULPHURIC ACID

INTRODUCTION

The behaviour of organic acid anhydrides in strong acidic media has been the subject of study for many years. In 100% sulphuric acid it has been shown that acetic anhydride and benzoic anhydride dehydrate the solvent[48,136] and form the corresponding carboxylic acidium ion ($RCO_2H_2^+$). However, in disulphuric acid acetic anhydride has been shown[46] to form the acyl ion ($R\overset{+}{C}O$). Formation of inter and intra molecularly proton exchanging protonated anhydride was indicated in solution of acetic anhydride and many other substituted acyclic anhydrides in an equimolar and even smaller amount of the super acid[49] HSO_3F-SbF_5-SO_2. In an excess of the solvent (super acid) cleavage of the protonated anhydride yielding both the carboxylic acidium ion and the oxocarbenium ion or acyl ion ($R\overset{+}{C}O$) has been shown For the dicarboxylic anhydrides several different modes of ionization in sulphuric acid have been shown. The ionization of succinic anhydride in 100% sulphuric acid has been represented[136] by the following reaction:



(61)

Later it was shown by Leisten[137] that only a simple 50% protonation of succinic anhydride in 100% H_2SO_4 occurs.

Recently, it has been shown that an equilibrium exists between the anhydride and the protonated anhydride[48] as given below:

$$R(COOH)_2H^+ \rightleftharpoons R(CO)_2O + H_3^+O \qquad (62)$$

None of the previous workers have tried to identify the species formed from the ionization of the dicarboxylic anhydrides in strong acidic media. Also none of the anhydrides mentioned above have so far been studied in chlorosulphuric acid. It was, therefore, considered worthwhile to study the behaviour of acetic, benzoic, maleic, succinic, phthalic and 3-nitrophthalic anhydrides in HSO_3Cl with a view to determining the mode and extent of ionization and to identifying the species being formed in solution by using conductometric, n.m.r. and i.r. spectroscopic techniques.

PREPARATION AND PURIFICATION OF REAGENTS

Purification of reagents:

Acetic anhydride (B.D.H., AnalaR) was redistilled and the fraction boiling at 137-138°C was collected.

Succinic anhydride (B.D.H.) was recrystallized from acetic anhydride (95-99%). The crystals were washed with dry ether and dried in vacuum at 100°C. It melted at 119.5°C.

Phthalic anhydride (B.D.H.) was recrystallized from chloroform and dried in vacuum at 110°C. It melted at 132°C.

Maleic anhydride (E.Merck) was recrystallized from chloroform and dried over phosphorus pentoxide. It melted at 42°C.

Synthesis of reagents:

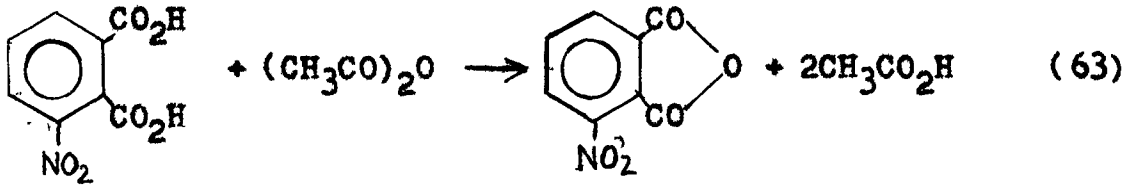
3-nitrophthalic anhydride[138] was prepared by the reaction of 3-nitrophthalic acid with acetic anhydride. The first step of the synthesis was to prepare 3-nitrophthalic acid as given below:

First Step 3-nitrophthalic acid: In a flask fitted with mechanical stirrer, 65 ml. of commerical sulphuric acid (sp.gravity 1.84) and 50 gm. of phthalic anhydride (B.D.H., Technical grade) were taken. The mixture was stirred and

heated gently on a water bath. When the temperature reached 80°C, heating was interrupted and 21 ml. of fuming nitric acid (Sp.gravity 1.51) was added slowly from a separatory funnel at such a rate as to maintain the temperature of the stirred mixture at 100-110°C. After the fuming nitric acid had been added, 90 ml. of concentrated nitric acid (Sp.gravity 1.42) was added. The mixture was then stirred and heated for two hours.

It was then allowed to stand over night and then poured into one litre of water. The solid mixture of 3- and 4-nitrophthalic acids was filtered by suction through a büchner funnel without a filter paper. The wet cake was then stirred thoroughly with 200 ml. of water which dissolved a large amount of 4-nitrophthalic acid. It was filtered off by suction and the wet cake was dissolved in 200 ml. of boiling water. This solution was filtered hot and stirred mechanically until crystallization started The crystals were filtered and air dried. The product melted at 210°C in a sealed tube.

Second Step 3 nitrophthalic anhydride: was prepared by reacting 3-nitrophthalic acid with acetic anhydride (B.D.H., AnalaR) according to the equation:



(63)

In a round bottom flask fitted with a reflux condenser 20 gm. of 3-nitrophthalic acid and 19 ml. of acetic anhydride were taken. The mixture was heated until the acid dissolved completely. The hot mixture was poured in a porcelain dish and allowed to cool. After a few minutes crystals were collected from the mother liquor. This was ground thoroughly and filtered. The crystals were washed with dry ether and then dried at 100°C. It melted at 163°C.

Benzoic anhydride[139] was prepared from the reaction of benzoic acid (B.D.H., commerical grade) and freshly distilled acetic anhydride (B.D.H., AnalaR). The following reaction takes place:

$$C_6H_5CO_2H + (CH_3CO)_2O \longrightarrow C_6H_5COOCOCH_3 + CH_3CO_2H$$

$$C_6H_5COOCOCH_3 + C_6H_5CO_2H \longrightarrow (C_6H_5CO)_2O + CH_3CO_2H. \qquad (64)$$

In a 1 litre flask fitted with a condenser and a dropping funnel 150 gm. of benzoic acid, an equivalent quantity of acetic anhydride (i.e 139 ml) and 1 ml. of syrupy phosphoric acid were taken. The mixture was very slowly heated. When 50 ml. of the distillate had been collected, 25 gm. of acetic

anhydride was further added and the distillation continued. The portion distilling at 120-130°C was discarded. Heating was continued until whole of the acetic acid formed in the reaction, was distilled off from the reaction mixture. The liquid distilling at 210-220°C under reduced pressure (20 m.m.) was collected. The crude benzoic anhydride was recrystallised from benzene and petroleum ether(b.p.40°-60°C). The product melted at 41.5°C.

TABLE - 61

Specific conductance of solutions of acetic anhydride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 58.8582 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1405
1.331	0.6610
1.568	0.7486
2.061	0.9512
2.522	1.1250
3.053	1.3090
3.648	1.5820
3.975	1.6980

EXPERIMENT - 2: 61.1266 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1399
0.1610	0.1889
0.3363	0.2520
0.7541	0.3990
1.5840	0.7739
3.0740	1.3330
3.9340	1.6490
4.566°	1.8720
5.202°	2.0790

TABLE - 62

Specific conductance of solutions of benzoic anhydride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 60.6618 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1455
0.570	0.3779
1.101	0.6125
1.502	0.7498
2.358	1.0940
3.014	1.3460
4.006	1.6970
4.451	1.8760

EXPERIMENT - 2: 80.8600 gm. of chlorosulphuric acid initially taken as solvent.

W x 10^2	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1455
0.235	0.2379
0.952	0.5425
1.346	0.7210
1.756	0.8750
2.759	1.2550
3.543	1.550°
4.211	1.746°
4.855	1.968°

TABLE - 63

Specific conductance of solutions of succinic anhydride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 57.7140 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1399
0.536	0.2450
1.322	0.4030
1.955	0.5320
2.778	0.6850
4.133	0.9441
5.304	1.1370
6.877	1.3810

EXPERIMENT - 2: 63.6126 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$K \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1405
0.225	0.1854
0.796	0.2910
1.592	0.4604
2.284	0.5820
3.466	0.8220
4.608	1.0160
6.066	1.2530
7.471	1.4450

TABLE - 64

Calculations for the determination of the dissociation constant (K_{BH^+}) of the conjugate acid formed in solutions of succinic anhydride in chlorosulphuric acid at 35°C.

C_w	C_s	α	$K_{BH^+} \times 10^2$ Moles.$Kg.^{-1}$
0.0132	0.0125	0.945	21.47
0.0159	0.0155	0.973	55.85
0.0196	0.0185	0.946	31.22
0.0228	0.0215	0.941	34.29
0.0278	0.0260	0.935	37.40
0.0347	0.0315	0.908	31.04
0.0413	0.0375	0.907	36.57
0.0461	0.0415	0.900	37.35
0.0530	0.0475	0.895	40.48
0.0607	0.0535	0.811	39.60
0.0688	0.0610	0.887	47.88
0.0747	0.0660	0.883	49.81

Average value of K_{BH^+} = 38.58 $\times 10^{-2}$ Moles.$Kg.^{-1}$

TABLE - 65

Specific conductance of solutions of phthatic anhydride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 63.3126 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1399
0.3325	0.2030
0.7467	0.2869
1.5630	0.4200
2.2580	0.5320
3.0900	0.6579
4.3960	0.8512
6.2260	1.0520

EXPERIMENT - 2: 71.5560 gm. of chlorosulphuric acid initially taken as solvent.

$\omega \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1399
0.1044	0.1609
0.4769	0.2274
1.0700	0.3395
1.9290	0.4759
2.6100	0.5802
3.7540	0.7791
5.1320	0.9065
7.2920	1.1300

TABLE - 66

Calculations for the determination of the dissociation constant (K_{BH^+}) of the conjugate acid formed in solutions of phthalic anhydride in chlorosulphuric acid at 35°C.

C_w	C_a	α	K_{BH^+} x 10^2 Moles.$Kg.^{-1}$
0.0156	0.0132	0.844	7.14
0.0193	0.0160	0.829	7.75
0.0226	0.0185	0.819	8.37
0.0261	0.0205	0.785	7.50
0.0309	0.0245	0.792	9.33
0.0375	0.0310	0.799	11.92
0.0439	0.0332	0.755	10.23
0.0513	0.0362	0.705	8.65
0.0623	0.0432	0.693	9.75
0.0729	0.0470	0.644	8.50

Average value of K_{BH^+} = 8.91 x 10^{-2} Moles.$Kg.^{-1}$

171

TABLE - 67

Specific conductance of solutions of 3-nitrophthalic anhydride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 78.8562 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1470
0.0155	0.1679
0.6786	0.2170
1.1590	0.2520
2.0830	0.3150
3.1650	0.3814
4.6180	0.4649
6.0830	0.5344

EXPERIMENT - 2: 61.1850 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1465
0.0456	0.1505
0.3864	0.1889
0.9169	0.2365
1.5030	0.2799
2.6160	0.3500
3.7760	0.4165
5.3730	0.4879
6.9920	0.5730

TABLE - 68

Calculations for the determination of the dissociation constant (K_{BH^+}) of the conjugate acid formed in solutions of 3-nitrophthalic anhydride in chlorosulphuric acid at 35°C.

C_w	C_a	α	$K_{BH^+} \times 10^2$ Moles.$Kg.^{-1}$
0.0068	0.0043	0.629	0.72
0.0092	0.0050	0.545	0.60
0.0116	0.0060	0.517	0.64
0.0150	0.0075	0.499	0.74
0.0208	0.0095	0.456	0.79
0.0262	0.0105	0.401	0.70
0.0316	0.0120	0.379	0.73
0.0378	0.0140	0.371	0.82
0.0462	0.0160	0.324	0.76
0.0537	0.0175	0.325	0.84
0.0608	0.0195	0.320	0.91
0.0699	0.0215	0.307	0.95

Average value of $K_{BH^+} = 0.77 \times 10^{-2}$ Moles.$Kg.^{-1}$

TABLE - 69

Specific conductance of solutions of maleic anhydride in chlorosulphuric acid at 35°C.

EXPERIMENT - 1: 61.6080 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.000	0.1509
0.376	0.1833
1.167	0.2314
2.048	0.2865
3.327	0.3709
5.123	0.4756
6.483	0.5285
8.426	0.6020

EXPERIMENT - 2: 59.9612 gm. of chlorosulphuric acid initially taken as solvent.

$w \times 10^2$	$\kappa \times 10^2$ ohm^{-1}cm^{-1}
0.0000	0.1505
0.1082	0.1609
0.6149	0.2030
1.6720	0.2661
2.5270	0.3150
4.4170	0.4304
5.5670	0.4865
7.1420	0.5530
8.8740	0.6195

TABLE - 70

Calculations for the determination of the dissociation constant (K_{BH^+}) of the conjugate acid formed in solutions of maleic anhydride in chlorosulphuric acid at 35°C.

C_w	C_s	α	K_{BH^+} x 10^2 Moles.$Kg.^{-1}$
0.0061	0.0030	0.487	0.28
0.0116	0.0045	0.385	0.28
0.0167	0.0065	0.388	0.41
0.0253	0.0090	0.356	0.49
0.0333	0.0115	0.345	0.61
0.0442	0.0140	0.316	0.65
0.0557	0.0167	0.300	0.72
0.0648	0.0185	0.285	0.74
0.0714	0.0195	0.273	0.73
0.0843	0.0215	0.255	0.74

Average value of K_{BH^+} = 0.57 x 10^{-2} Moles.$Kg.^{-1}$

DISCUSSION

Results of the conductometric, n.m.r. and i.r. spectroscopic studies on solutions of acetic, benzoic, succinic, phthalic, maleic and 3-nitrophthalic anhydrides have been summarized in Tables-71,72 and 73 respectively.

Acetic and benzoic anhydrides gave stable and highly conducting (γ= 2.00) colourless solutions in chlorosulphuric acid. Their ionization could equally well be represented by equation (65) or (66) as given below:

$$(RCO)_2O + 2HSO_3Cl \rightleftharpoons R\overset{\oplus}{C}O + RCO_2H_2^{\oplus} + 2SO_3Cl^{-} \quad (65)$$

$$(RCO)_2O + 4HSO_3Cl \rightleftharpoons 2RCO_2H_2^{\oplus} + S_2O_5Cl_2 + 2SO_3Cl^{-} \quad (66)$$

$$R = CH_3 \text{ or } C_6H_5$$

Ionization after equation (65) results in the formation of two species viz. oxocarbenium ion or acyl ion ($R\overset{\oplus}{C}O$) and the carboxylic acidium ion ($RCO_2H_2^{\oplus}$) and would thus require the appearance of two separate CH_3 or C_6H_5 signals in the n.m.r spectrum. In the n.m.r. spectra of solutions of acetic anhydride and benzoic anhydride in HSO_3Cl however, only one peak is observed at 2.98δ in the former case and at 8.50δ in the latter. This observation rules out ionization represented by equation (65). In super acidic

TABLE - 71

Average value of γ and K_{BH^+} calculated from specific conductances of the compounds in chlorosulphuric acid at 35°C.

Compound	γ	$K_{BH^+} \times 10^2$ Moles.Kg.$^{-1}$
Acetic anhydride	2.00	-
Benzoic anhydride	2.00	-
Succinic anhydride	0.90	38.58
Phthalic anhydride	0.75	8.91
3-nitrophthalic anhydride	0.45	0.77
Maleic anhydride	0.35	0.57

TABLE - 72

Chemical shifts in p.p.m. for compounds in $CDCl_3$ and HSO_3Cl using T.M.S. as external reference, at 25°C.

Compound	Solvent		Δ^+
	$CDCl_3$	HSO_3Cl	
Acetic anhydride	2.05	2.98	0.93
Benzoic anhydride	7.59	8.58	0.99
Succinic anhydride	3.06	3.60	0.54
Phthalic anhydride	8.00	8.41	0.41
3-nitrophthalic anhydride	8.46*	8.90	0.44
Maleic anhydride	7.13	7.53	0.40

* peak obtained in acetone

+ difference of the δ value observed in HSO_3Cl with that in $CDCl_3$ or acetone.

TABLE - 73

I.r. frequencies in cm^{-1} of protonated and unprotonated acid anhydrides between 1500 cm^{-1} and 2200 cm^{-1}

Compound	Solvent	
	Nujol	HSO_3Cl
Acetic anhydride	1748,1824*	1605 b.s
Benzoic anhydride	1689,1790	1600 b.s
Succinic anhydride	1788,1850	1730 b.s
Phthalic anhydride	1760,1839	1720 b.s
3-nitrophthalic anhydride	1680,1720	1650 b.s
Maleic anhydride	1775,1850	1740 b.s.

* taken from ref.103

b.s = broad and strong

media (SbF_5-HSO_3F) a sharp peak at 3.12 δ for acetic acid and the multiplet centered at 8.00 δ for benzoic acid solutions have been attributed[96] to the methyl and phenyl protons of the carboxylic acidium ion. It has been shown that the methyl protons of the acyl ion ($RC\overset{+}{O}$) formed in the solution of acetic acid and acyl halides in disulphuric acid[100] appears at about 4.00 δ . The peak observed at 2.98 δ and 8.50 δ for solutions of acetic and benzoic anhydrides respectively, is therefore, assigned to the methyl and phenyl protons of the carboxylic acidium ion. The n.m.r data are thus consistent with the mode of ionization represented by equation (66) where the formation of only one cationic species ($RCO_2H_2^+$) is indicated. The peak due to the conjugate acid proton ($C=O\overset{+}{H}$) could not be observed in both the cases due to a rapid proton exchange with the solvent proton as evidenced by the broad solvent peak.

The formation of only the carboxylic acidium ion in both the cases is further confirmed by the i.r. spectroscopic studies. The two carbonyl stretching frequencies at 1748 $cm.^{-1}$ and 1824 $cm.^{-1}$ for pure acetic anhydride[103] and at 1689 $cm.^{-1}$ and 1790 $cm.^{-1}$ for benzoic anhydride in nujol (Table-73) disappeared in their chlorosulphuric acid solutions. Instead a strong broad band at 1605 $cm.^{-1}$ for

acetic anhydride and at 1600 $cm.^{-1}$ for benzoic anhydride is observed and is attributed to the C=O stretching vibration of the protonated carbonyl group of the carboxylic acidium ion. The bands at 1618 $cm.^{-1}$ and 1552 $cm.^{-1}$ observed[102] in the solution of acetic acid in sulphuric acid has been suggested to be the characteristic of the protonated carbonyl group of the acetic acidium ion ($CH_3CO_2H_2^+$). Hoshino and coworkers[101] have also observed a strong broad band at 1600 $cm.^{-1}$ for acetic acid solution in H_2SO_4 and at 1603 $cm.^{-1}$ for benzoic acid solution in D_2SO_4. They have assigned these to the antisymmetric stretching vibration of the protonated carbonyl group of the acidium ion. The assignment of the peaks at 1600 $cm.^{-1}$ and 1605 $cm.^{-1}$ to the C=O stretching vibration of the acidium ion ($RCO_2H_2^+$) is consistent with the observations of Hoshino and coworkers. The absence of the acyl ion (RCO^+) in solutions of acetic and benzoic anhydrides in HSO_3Cl is confirmed by the absence of the ($C\equiv O^+$) stretching vibration observed at about 2200 $cm.^{-1}$ in solutions of acetic acid, acetyl halides and benzoyl chloride in disulphuric acid.[100]

All the other acid anhydrides viz. succinic, phthalic, 3-nitrophthalic and maleic anhydrides have been found to behave as weak bases ($\gamma < 1.0$) in chlorosulphuric acid (Figures 16 and 17). The basic dissociation constant K_{BH^+} of the corresponding conjugate acid has been calculated by using

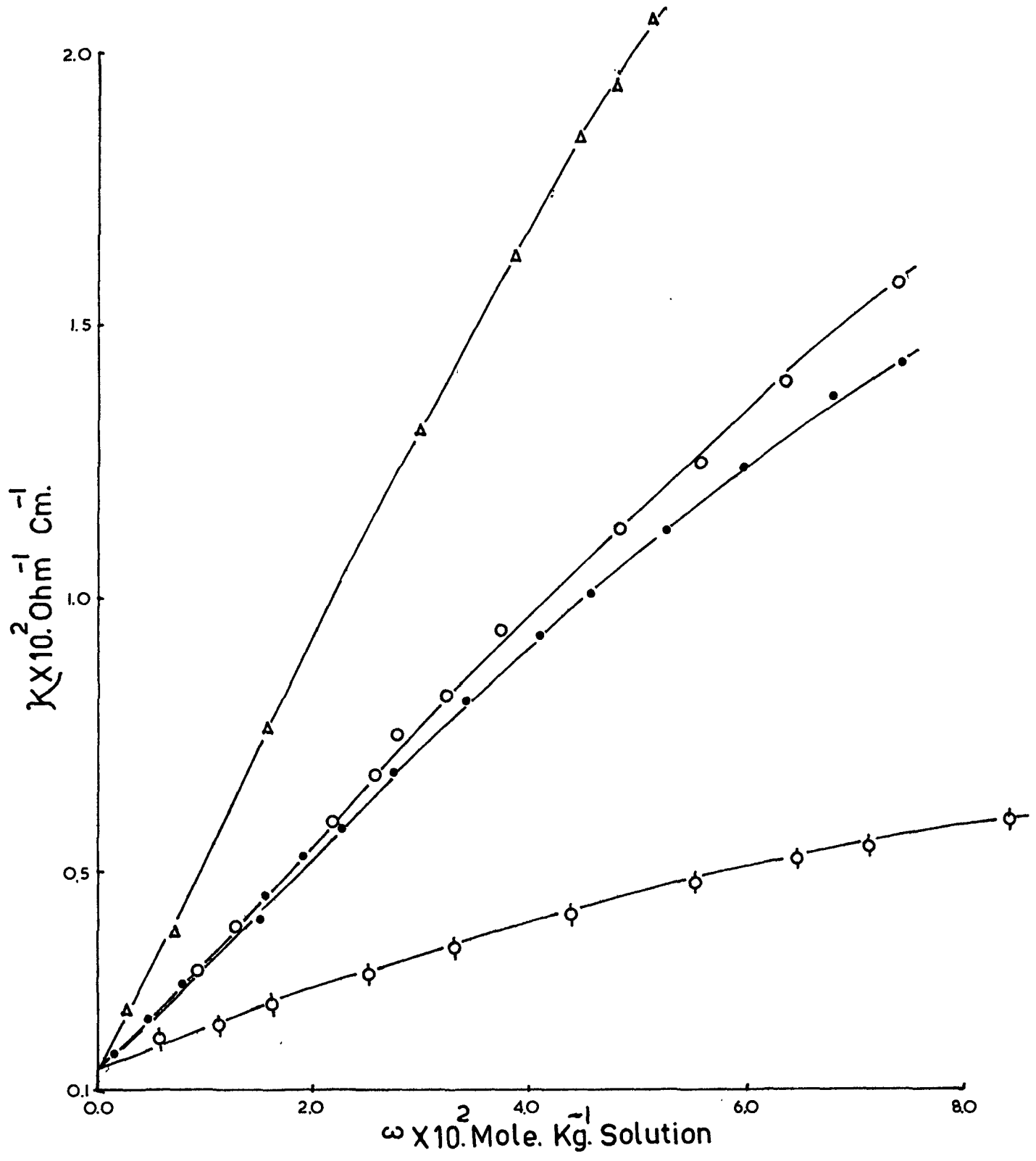
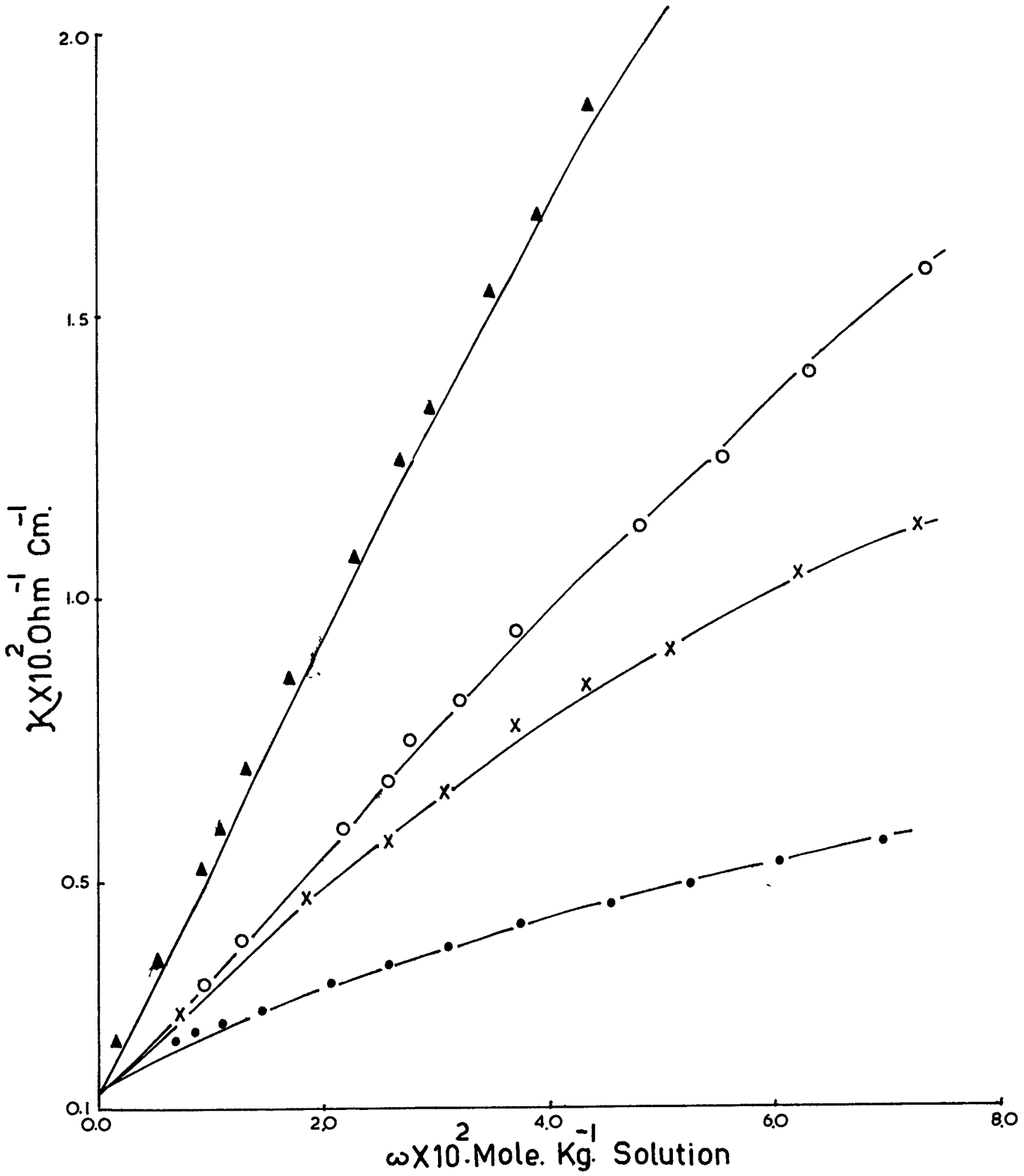

2.0
1.5
1.0
0.5
0.1
0.0
2.0
4.0
6.0
8.0
κ X 10^2 Ohm^-1 cm.^-1
ω X 10^2 Mole. Kg.^-1 Solution
Δ ACETIC ANHYDRIDE
O POTASSIUM CHLORIDE
• SUCCINIC ANHYDRI DE
ϕ MALEIC ANHYDRIDE

Fig.16



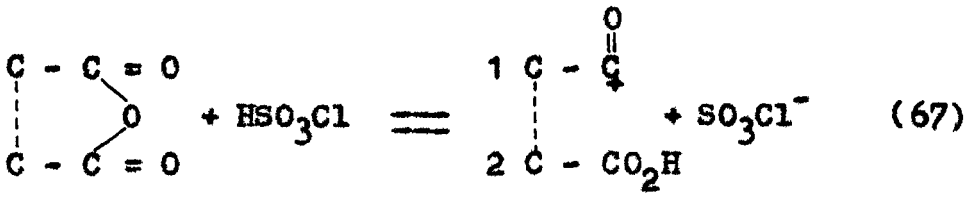
▲ BENZOIC ANHYDRIDE
O POTASSIUM CHLORIDE
X PHTHALIC ANHYDRIDE
• 3-NITROPHTHALIC ANHYDRIDE

Fig. 17

equation (56) described in Chapter VI. The average value of K_{BH^+} for succinic, maleic, phthalic and 3-nitrophthalic anhydrides thus obtained by using equation(56) is shown in Table-71.

The results of the conductometric measurements of the above mentioned dicarboxylic anhydrides could be consistent with any of the following three modes of ionization:

(i) There may be an incomplete formation of the acyl ion (A) according to equation (67) as follows:

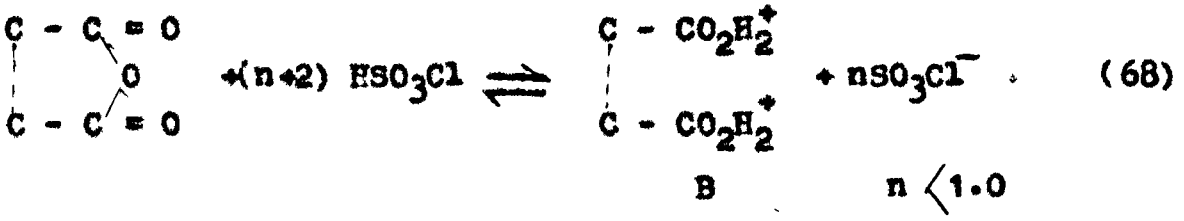


(67)

A

The proton at carbon atom 1 and 2 of (A) would no more be identical and should show two different signals in the n.m.r. spectrum. Furthermore, in the i.r.spectrum there should be a band at around 2200 cm^{-1} characteristic of the ($C\equiv O^+$) stretching vibration of the acyl ion.[100] The presence of only one kind of protons in the n.m.r.spectra and the absence of a band around 2200 cm^{-1} in the solutions of these dicarboxylic anhydrides in HSO_3Cl rule out ionization according to equation(67).

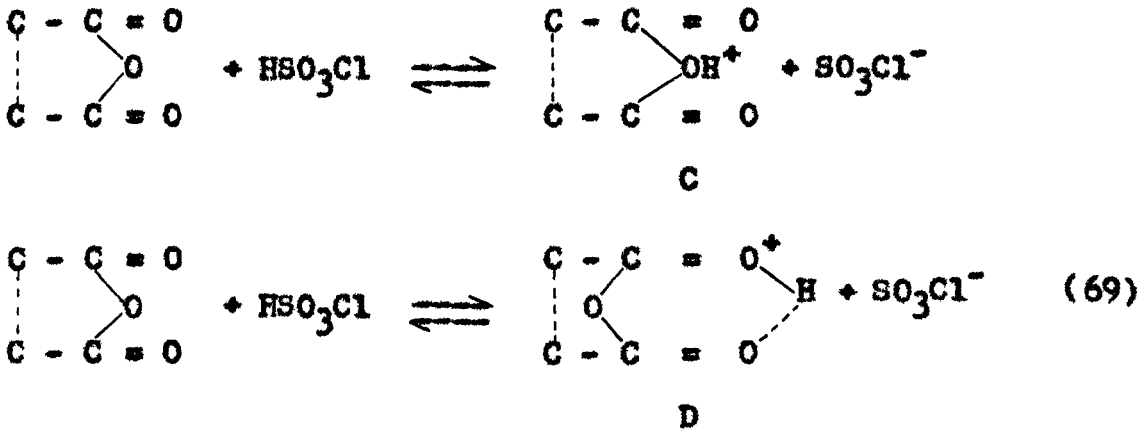
(ii) Ionisation producing the partially protonated carboxylic acidium ion (B) according to equation (68) is ruled out on the grounds that in the i.r. spectra of these compounds in HSO_3Cl the band at around 1600 cm^{-1} characteristic of the carboxylic acidium ion is absent.



(68)

The n.m.r. spectra of the above mentioned compounds obtained in HSO_3Cl and $CDCl_3$ supported this as in HSO_3Cl solution the shift in the adjacent methylene and phenyl proton peaks was about 0.50δ in these cases. This shift is only half as much as that observed in the case of methyl and phenyl protons of acidium ions ($RCO_2H_2^+$) formed in the case of acetic and benzoic anhydrides (Table-72).

(iii) There may be a partial protonation either at the ethereal oxygen atom resulting in the formation of the species (C) or at the carbonyl oxygen resulting in the formation of an intramolecularly hydrogen bonded protonated anhydride (D).



C

D

One can easily differentiate the species (C) from (D) by examining the change in C=O and C-O-C stretching frequencies of the solutes in HSO_3Cl from that observed in unprotonated form. The C-O-C band is unfortunately obscured by a broad solvent band in this region and thus the only way to decide the site of protonation is to examine the change in the carbonyl (C=O) stretching frequency. Protonation at ethereal oxygen should not result in any significant change in the C=O stretching frequency. However, a strong broad band shifted to lower wave-number from its position in nonpolar medium is observed. This marked shift in the C=O stretching vibration to lower frequency clearly points to the protonation at the carbonyl groups. Since a band attributable to the unaffected C=O groups is not observed, the extent of protonation in these compounds is very small ($\gamma < 1.0$), it is proposed that one of the carbonyl group is protonated and the other is hydrogen bonded with it yielding the species (D).

The formation of species (D) is further supported by the n.m.r. spectra of the solutions of succinic, maleic, phthalic and 3-nitrophthalic anhydrides in HSO_3Cl and $CDCl_3$. In these cases a downfield shift of about 0.50δ only is noted. This may presumably be due to the formation of a species in which the positive charge is more delocalized than in acidium ion ($RCO_2H_2^+$) formed by acetic and benzoic anhydrides in HSO_3Cl where a down-field shift of about 1.00δ is noted. This observation suggests the formation of the protonated species (D) where the proton attached to one carbonyl group is intramolecularly exchanging with the other carbonyl group as has been suggested by Olah and coworkers in the case of acyclic anhydrides in super acidic media.[49]

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